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COLLOIDS

AND THE

ULTRAMICROSCOPE

A MANUAL OF

Colloid Chemistry and Ultramicroscopy

BY

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AUTHORIZED TRANSLATION

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PREFACE TO THE ENGLISH EDITION

THE expectation that this book would arouse the interest of a wider circle has been agreeably fulfilled. I am glad to be able to state that Mr. Jerome Alexander, of New York, has undertaken to translate the book because of interest in its contents, and has carried out the work carefully and conscientiously. I have myself read over the whole translation and found it in excellent accord with the original text.

In so far as concerns the experimental basis for answering the fundamental questions of Colloid Chemistry, there is but little to be added to the German edition. In but few places has it become necessary to amplify the statements and extend the text because of later publications.

May the English edition receive the same friendly reception as the German edition.

R. ZSIGMONDY.

GÖTTINGEN, November 14, 1908.

TRANSLATOR'S PREFACE

After discussing the basic principles governing the colloidal condition, and the classification of colloids, and reviewing the most important work already done in this field, the author describes the development (upon the principle originally conceived by himself) of the ultramicroscope, which carries our range of vision well towards molecular dimensions; and he furthermore gives a detailed account of his own valuable pioneer researches with the new instrument.

Giving as it does an actual insight into a sphere heretofore beyond the range of direct observation, the ultramicroscope has proven to be a powerful weapon with which to attack numerous problems confronting the chemist, the physicist, and the biologist; and it will be of special value in deciding many mooted questions in theoretical and in technical colloid chemistry.

As the far-reaching ramifications of colloid chemistry are better understood, its importance and the applicability of its principles to a great variety of industrial problems, become more and more evident. There might, for example, be mentioned agriculture, tanning, dyeing; rubber, cement, ceramics; soaps, photography, sugar—in fact, almost every industry is directly or indirectly involved. Professor Zsigmondy's work will, therefore, be of vital interest not only to scientists concerned with theoretical

questions, but also to chemists, engineers, and others controlling technical processes. To physiological chemists and physicians it is indispensible.

I must express my sincere thanks to Prof. Zsigmondy and also to Alexander D. Ross, M.A., B.Sc. (lecturer on Natural Philosophy in the University of Glasgow), both of whom read over the original manuscript of the translation and made valuable suggestions. In the English edition besides some additions to the text, there are included two beautiful colored plates originally published in Professor Zsigmondy's paper on "Colloid Chemistry."

JEROME ALEXANDER.

NEW YORK, February 24, 1909.

PREFACE TO THE GERMAN EDITION

SOME of the conclusions and observations herein set forth were originally intended for the Zeitschrift für physikalische Chemie; however, as the method of rendering visible ultramicroscopic particles which were developed by Siedentopf and myself, has awakened the interest of a larger circle, I have decided to make readily accessible to the representatives of other branches of science the results of my ultramicroscopic investigation of fluids, and the experiments associated therewith; all the more so because they may be of some use to other workers in the same field. Another reason that led me to take this step was the fact that the problem I attacked is of interest not only to the physicist and the chemist, but to scientists in general.

It will be shown by a number of examples how the properties of a solid—metallic gold—change with its progressive subdivision, especially if the subdivision be carried as far as possible, to a degree approaching molecular dimensions; and as near as may be the size and properties of the individual particles in each case are accurately given.

As will be seen in the following chapters, the problem is intimately connected with the question of the nature of colloidal solutions, the latter in fact being the starting point of this investigation.

The paucity of our knowledge on this subject is shown by the discussion of the question whether colloidal solutions are homogeneous or heterogeneous, and whether there is or is not progressive transformation from colloidal to crystalloidal solution. As a preliminary discussion shows that the words "solution" and "suspension" are by no means synonymous, it is necessary, in order to pave the way, to consider what these expressions really mean.

The title of this book, "Zur Erkenntnis der Kolloide," might lead to the belief that I intended to go into the structure of hydrogels or jellies. Chapter XXI contains some remarks on this subject. When working in a wide field, however, it is best to proceed from the simple to the complex. Solutions of colloids are of a simpler nature than jellies; they contain to a certain extent the structural units of the latter, and wherever before coagulation begins, the appearance of ultramicroscopic particles is observed, it may be taken for granted that these are constituents of the hydrogel. Finally, when we have acquired more intimate knowledge of the actual constitution of such colloidal solutions, we can then successfully theorize regarding the ultimate structure of jellies which does not admit of direct observation.

But the constituent particles of hydrosols, which I have just compared to structural units, show such variation in size, constitution, and properties, that it is necessary at the outset to confine ourselves to one especially simple case. As already intimated, the colloidal solutions of metallic gold have been chosen. The minute particles of gold composing them, their formation, their relation to each other, and to the particles of other colloids, are all closely considered. Reference to earlier work will show that they are not indifferent to the action of other

colloids, and that when they are mixed with other colloids, products are often produced which have been in the past frequently mistaken for chemical compounds.

In addition I have given, in more or less detail, an account of my ultramicroscopic investigations on various hydrosols, and also of the work already published by other investigators.

On seeing the variety of these elementary relations, it will at once be manifest that in the study of the colloids we have outlined an enormous scientific structure, whose foundation is as yet scarcely begun.

R. ZSIGMONDY.

JENA, May, 1905.

CONTENTS

INTRODUCTION

PAGE

Introduction 1

CHAPTER I

Limitation of the Field 11

CHAPTER II

Classification of Hydrosols according to Two Different Points of View 19

CHAPTER III

History of the Irreversible Colloids 30

CHAPTER IV

Facts Pointing to the Homogeneity of Gold Hydrosols. Development of Ultramicroscopy 95

CHAPTER V

Description of the Apparatus for Making Visible Ultramicroscopic Particles 103

CHAPTER VI

Certain Terms often Used Herein 109

CHAPTER VII

PAGE

Principles of the Ultramicroscopic Investigation of Fluids 111

CHAPTER VIII

Preparation of Colloidal Gold Solutions 124

CHAPTER IX

Ultramicroscopic Examination of the Solutions of Gold .. 129

CHAPTER X

Motion of the Gold Particles 134

CHAPTER XI

Size and Color of the Particles 141

CHAPTER XII

The Color Change of Colloidal Gold 144

CHAPTER XIII

The Precipitation and Protection of Colloidal Gold 147

CHAPTER XIV

Filtration Experiments 153

CHAPTER XV

The Size of the Gold Particles Compared with the Size of Other Bodies 157

CHAPTER XVI

PAGE

Superior and Inferior Limits of the Size of the Particles 160

CHAPTER XVII

Amicroscopic Nuclei in Colorless Ruby Glass 165

CHAPTER XVIII

General Remarks Concerning Metal Hydrosols 175

CHAPTER XIX

Ultramicroscopic Examination of Certain Solutions and Suspensions 188

CHAPTER XX

Ultramicroscopic Investigations from the Publications of Other Scientists 198

CHAPTER XXI

On the Formation of Hydrosol and Hydrogel 212

Recapitulation 236

COLLOIDS AND THE ULTRAMICROSCOPE

INTRODUCTION

Regarding Solution and Homogeneity. The original conception of the word "solution," and the one still extant, does not completely coincide with that developed from the generalization of the laws of gases.

As considerable misunderstanding may arise by using the term "solution" to express different ideas, a few words on this subject may not be amiss.

Solutions are more easily described by limitation than by definition. Originally they included solutions not only of crystalloids, but also many of the earlier known colloids. Graham included for instance solutions of albumen, glue, rubber, ferric oxid, Prussian blue, etc., and because of its uniform appearance Berzelius considered the purple of Cassius to be a solution. Ordinarily we speak of dilute aqueous solutions of zinc chlorid and ferric chlorid. although these solutions are partially hydrolyzed and lack homogeneity.

An example of an old definition of "solution" is found in Felhing's "Handwörterbuch der Chemie":

"Solution is the equal distribution of a body in a liquid, the resulting mass being in all parts homogeneous and fluid enough to form drops. According as the dissolved body is solid, fluid, or gaseous, the product is termed a

solution (in the restricted sense of the word), a mixture, or an absorption."

Ostwald and Nernst also define solution as a homogeneous mingling,[1] a physical mixture,[2] a homogeneous phase.[3] Consequently homogeneity is even now regarded as the distinguishing characteristic of solutions.

Because of the brilliant results following the general application by van't Hoff of the laws of gases, physical chemists came to regard these laws as typical attributes of solutions, although as enunciated they apply only to solutions in the more limited sense, viz., those of a crystalloidal nature. As characteristic properties of crystalloid solutions, may be mentioned: diffusibility, osmotic pressure, the capability of the solute (in the case of solids) to crystallize from supersaturated solutions.

Regarding the above as the most important characteristics of solutions,[4] these scientists must have naturally considered the question whether those mixtures which completely or partially lack these characteristics (colloidal solutions or hydrosols) could be classed as solutions at all.[5]

[1] Ostwald, Grundriss der allg. Chem., 2d ed., p. 119.

[2] Nernst considers solutions to be physical mixtures, and defines them as complexes of different substances, in every part physically and chemically homogeneous. Theoret. Chem., 3d ed., p. 99.

[3] Ostwald, Grundriss, 3d ed., p. 313.

[4] Some scientists apparently failed to observe the fact that in addition to the conception of solution as used by them, there exists another with a much wider meaning which is in general use. I do not therefore consider it necessary to put the word "solution" in quotation marks when speaking of colloidal solutions.

[5] It might here be mentioned that research on this point has lead to the conclusion: typical colloidal solutions are not solutions. It will, of course, be seen that this only means that typical colloidal solutions are not *crystalloidal* solutions, which statement hardly expresses any new idea of importance. The physico-chemical investigation of colloids however, has lead to most important results, and very largely extended our knowledge of them.

The definitions, however, are not based upon the properties above referred to, but give homogeneity as the most important characteristic. Because of this state of affairs the moot question as to the nature of colloidal solutions hinges on the question of their *homogeneity* or *heterogeneity*. This very circumstance has lead to an important extension of our knowledge. We must therefore next consider the concept "*homogeneity*."

In his book: "Heterogeneous Equilibrium," Bakhuis Roozeboom [1] states:

"We call a system homogeneous if all its mechanically separable parts show the same chemical constitution and the same chemical and physical properties.

"Gases or liquids which have been well mixed possess this homogeneity of constitution because of the smallness of molecules and the grossness of our means of observation."

We still are unable to observe directly particles the size of a crystalloid molecule. However, by means of the Faraday-Tyndall convergent beam of light, we are able in an indirect manner, with the aid of the Nichol prism, to demonstrate the existence of very small boundary planes, and therefore of particles of unusually small size. As Bredig [2] has already pointed out, Tyndall's method is the most sensitive for the recognition of the lack of optical homogeneity. By this method, as we shall see, we can detect smaller quantities of substances than by spectrum analysis; but just because of its enormous sensitiveness, the most extreme care must be taken in forming conclusions as to the nature of a solution, upon the basis of the results of an examination by it.

[1] B. Roozeboom, Die heterogenen Gleichgewichte, Part I, p. 9, Braunschweig, 1901.

[2] Bredig, Anorganische Fermente, Leipzig, 1901, p. 21.

This I pointed out several years ago.[1] Recently a similar view was advanced by Konowalow,[2] who, because of its enormous sensitiveness, denies the value of the Tyndall method, and regards solutions in the critical state, and colloidal solutions as well, to be homogeneous solutions, which owe their inhomogeneity to a partial separation of the substance otherwise homogeneously dissolved.

Consequently Konowalow took the stand that there are homogeneous solutions in which, as compared with crystalloid solutions, the work necessary to separate solvent and solute is excessively small.[3]

This standpoint coincides to some extent with the one I have formerly taken.[4] Because of observations, to which we will later on return, I regarded optical inhomogeneity as an incidental characteristic of colloidal solutions, attributing their opalescence (Lichtzerstreuung) to the presence of a smaller number of larger particles, while I regarded the bulk of the colloid as being in homogeneous solution.

From the following remarks it will be evident that the importance ascribed to the optical inhomogeneity of colloidal solutions by Faraday, Picton and Linder, Spring, Bredig, and others, is well founded. Furthermore, we will find confirmation for the compromise view of Lobry de Bruyn, that a particle the size of a starch molecule

[1] Zeitschr. f. physik. Chem., Vol. XXXIII, p. 64.

[2] Konowalow, Drude's Ann., Vol. X, p. 360–392, 1903, and Vol. XII, p. 1160–64, 1903.

[3] The cause of opalescence in liquids, according to Konowalow, is the "very fine dust," which is found everywhere. The reason it is so strongly marked in the critical state and in colloidal solutions, is due to the fact that in these cases the vapor pressure, as well as the osmotic pressure, is practically independent of the constitution.

[4] Zsigmondy, Liebigs Ann., Vol. CCCI, p. 53; Zeitschr. f. physik. Chem., Vol. XXXIII, p. 64.

can *within its own mass* diffract light of sufficient intensity to be observed.

The method of Tyndall was further extended by means of a method developed by H. Siedentopf and myself, of rendering visible ultramicroscopic particles.[1] With its aid we can readily determine whether the inhomogeneity recognized by the Tyndall method is due to larger or to smaller particles. It also gives us within certain limits an idea of the size and color of the particles, and information furthermore if they are at rest or in motion. By this method we can even determine the major size limit of individual particles, which are beyond the bounds of visibility, providing we first fix the limit of ultramicroscopic visibility of the particles of the body in question.

The research described herein, made according to this method, has shown, in conformity with prior publications,[2] that the optical inhomogeneity which appears as a distinct haze when the particles are about 100 $\mu\mu$ in size becomes less and less as the particles become smaller; that fluids containing particles measuring 20 $\mu\mu$ or less appear clear by ordinary daylight,[3] and that the optical inhomogeneity recognizable by the method of Tyndall is still to be seen with particles approaching the size which the kinetic theory of gases ascribes to the molecules of crystalloids, but vanishes upon further subdivision.

Hence solutions of crystalloids, unless they contain very

[1] Siedentopf and Zsigmondy, Drude's Ann., Vol. X, pp. 1–39, 1903. See also Chapter VI.

[2] Zsigmondy, Zeitschr. f. Elektrochemie, Vol. VIII, pp. 684–687, 1902; Siedentopf and Zsigmondy, Drude's Annal., Vol. X, pp. 30–39, 1903. H. Siedentopf, Journ. Roy. Microscop. Soc., pp. 573–578, 1903.

[3] These facts apply to gold; with other substances *noticeable* opalescence vanishes much sooner.

large molecules[1] or are reduced to hydrosols by colloid formation,[2] should appear optically homogeneous when examined with the convergent beam of light (Lichtkegel.)

Since, therefore, the hypothetical molecules of crystalloids of low molecular weight escape direct observation because of their small size, and the best optical instruments that we have at present are powerless against them; and since some crystalloid solutions appear perfectly homogeneous optically, the question naturally arises if we cannot by other means observe the lack of homogeneity which the molecular theory presumes to exist in every solution.

A means to this end might be the use of light waves of the greatest specific intensity, or else of ultraviolet light for illumination, in conjunction with the photographic plate to observe the diffracted light.

It may be that we can also make use of differences of density which escape direct observation, by the application of mechanical force to a separation of the constituents.

Some recently published work along this line by van Calcar and Lobry de Bruyn should be of great interest. These two Dutch investigators, by the action of centrifugal force on salt solutions (KI, KCyS, etc.), have been able to produce a considerable change of concentration, and in the case of a saturated solution of Glaubers salt, were even able to force three eighths of the dissolved salt to crystallize at the periphery of the rotating vessel.[3] Van Calcar and Lobry de Bruyn regard this fact as new

[1] Lobry de Bruyn and Wolff, Rec. Trav. chim. Pays-Bas., Vol. XXIII, p. 155, 1904.

[2] Spring, Bull. d l'Acad. roy. de Belgique, No. 4, pp. 300–315, 1899.

[3] v. Calcar and Lobry de Bruyn, Rec. Trav. chim. Pays-Bas., Vol. XXIII, pp. 218–223, 1904. Earlier work in this field was done by Th. des Coudres, Bredig, Colley, and Quincke.

evidence of the continuity of the transition from colloid to crystalloid solution, which idea had been repeatedly advanced by the latter as well as by Picton and Linder. To me these experiments seem to support the view that even the homogeneous solutions of the crystalloids are not in a strict sense homogeneous, for in no fluid which is physically and chemically uniform in all its parts, and which therefore has the same specific gravity in every conceivable little section, could such a difference of concentration be produced, no matter how great the speed of rotation of the centrifuge.

Finally, we must mention that, according to Lord Rayleigh, part of the polarized blue light of the sky may be attributed to the diffraction of sunlight by the molecules of the atmosphere.[1] There are, therefore, media which, although in small volume they may appear entirely homogeneous and optically clear, may nevertheless possess an inhomogeneity so small that it can be observed only by looking through a depth comparable to the height of the atmosphere.

After these remarks, on returning to the definition of solution, we see that, just as other investigators have said, when solutions are spoken of as homogeneous distributions, mixtures, etc., it cannot be meant that they are absolutely homogeneous mixtures. If such great homogeneity is demanded of solutions that we can detect no inhomogeneity in them by our most sensitive methods, we would thereby exclude altogether from this classification solutions[2] not only of many colloids, but also of numerous crystalloids, for example, fuchsin, ferric chlorid, chromic chlorid,[3]

[1] Philos. Mag., Vol. XLVII, pp. 375-384, 1899.

[2] It need hardly be said that polarized diffraction is referred to, not fluorescence.

[3] Spring, loc. cit., Picton and Linder, Journ. Chem. Soc., Vol. LXI, pp. 114-136.

saccharose, raffinose,[1] and solutions in the critical state.[2] We would thus run a risk of reducing the sphere of solutions every time we increase the sensitiveness of our methods of investigation. This danger can be easily avoided if we use the word "solution" in its usual chemical acceptation, meaning thereby subdivisions which appear clear in ordinary daylight, and which cannot be separated into their constituents by the ordinary mechanical means of separation (filtration and decantation). The word solution will be used here in this sense. The question of the heterogeneity of colloidal solutions seems rather to resolve itself into the question of the heterogeneity of solutions in general; and this standpoint may lead to many investigations of the highest importance.

Regarding Suspension and Colloidal Solution. While most chemists regard suspension as a coarse mechanical mixture, the solid or semi-solid parts of which can be separated from the fluid by decantation and filtration,[3] some physicists—Faraday for example—went much further, and considered as suspensions the smallest particles that can by any manner of means be recognized optically, *even if the individual particles cannot be seen.* They knew not how far this brought them into the domain of the colloidal solutions of the chemist, the physiologist, and the physician.

While several investigators differentiate between suspensions and emulsions, according as the subdivided substance is solid or fluid, others have made no such dis-

[1] Lobry de Bruyn and Wolff, Rec. Trav. chim. Pays-Bas, Vol. XXIII, p. 155, 1904.

[2] Konowalow, loc. cit.

[3] Examples: Suspended stannic acid, alumina, etc.; suspended ferric oxid in contrast to: colloidally dissolved stannic acid, alumina; solutions of colloidal ferric oxid.

tinction. According to Quincke,[1] suspensions contain solid or fluid particles, while emulsions contain only fluid particles, or else solid floating particles that are coated with a thin oily skin.

From what precedes,[2] it is evident that there is no uniform conception of "suspension," and that therefore, because the multifarious meaning of this word can easily lead to misunderstanding, even to the extent of considering as suspensions only the coarse mechanical ones, we must hold as erroneous the definition in most general use, that colloidal solutions and also colloidal metals are suspensions.[3]

I believe that all misunderstanding could be avoided if in this definition we use the word *subdivision*[4] instead of *suspension*. No one could object to the conception of colloidal solutions or hydrosols as very fine subdivisions, especially as this involves no assumption regarding the nature of the aggregation of the material subdivided, or the forces affecting the individual particles, or their stereometric nature, or their size and limits. These are questions that cannot be answered by general definition or by hypotheses, but each case must be differentiated by experimentation, which will make the investigation of

[1] Drude's Ann., Vol. IX, pp. 1009 and 1010, 1902.

[2] Here might be mentioned the hypothesis of Lemery (Cours de chimie, Leyden, 1716) which at present seems to us extremely odd, that gold chlorid solution is a suspension of gold particles carried by a network of aqua regia. (See Ostwald, Lehrb. der allgem. Chem., 2d ed., Vol. II, 2, p. 5.)

[3] Cf. B. A. Müller, Zeitschr. f. anorg. Chem., Vol. XXXVI, p. 340, 1903.

[4] The term "subdivision" is frequently misunderstood. It is a generic term, "suspension" and "solution" being specific terms included within it, and it does *not* express any definite degree of fineness, as is commonly supposed.

colloids the theme of a new, far-reaching science, built upon the present promising foundation.

We may further characterize colloidal solutions and distinguish them in an unobjectionable manner from crystalloidal solutions, by incorporating into the definition of the former the characteristic noted by Graham, who showed that colloidal solutions lack the property (or else possess it very slightly) of diffusing through parchment membranes.[1]

A safe distinction between coarse mechanical suspensions and colloidal solutions is that the latter have a more complete and thorough mixture of the constituents, and possess greater homogeneity, as compared with the former. The claim that colloidal solutions must show osmotic pressure, small though it may be, in order to be called solutions at all, does not appear to me to be essential, for it adds but little to the characteristics of the hydrosols, whether their solutions possess measurable osmotic pressure or not.

In this book we will designate as suspensions only the coarser subdivisions of solids, such as fine powders which undergo sedimentation. Finer subdivisions which no longer settle, will on the other hand be called colloidal solutions if they exhibit the other essential characteristics of such solutions.

[1] There might also be incorporated into the definition, the criterion noted by Bredig (Anorganische Fermente) "that the work necessary to separate solvent and solute is extremely small in comparison with crystalloid solutions."

CHAPTER I

LIMITATION OF THE FIELD

1. Limitation as to Crystalloidal Solutions

THE chief characteristics distinguishing colloidal from crystalloidal solutions, have already been given by Graham. According to him colloidal solutions are distinguished from crystalloidal solutions by their small diffusibility, and the concomitant inability of the majority of them to pass through parchment membranes or jellies. (See Chapter III.)

Numerous other distinguishing characteristics were noted by Graham as well as by other investigators, and Bredig[1] has done us the service of compiling them and adding some new ones.

According to Bredig solutions of crystalloids and colloids may be distinguished by means of: (*a*) diffusibility; (*b*) the work necessary to remove the solvent; (*c*) electrical migration; (*d*) coagulation; (*e*) absorption; (*f*) irreversible changes of constitution and hysteresis; (*g*) impermeability to other colloids; (*h*) optical inhomogeneity; (*i*) electrical formation of sols.

It is evident from this brief resumé that there are many ways of distinguishing colloids from crystalloids. Notwithstanding this, no sharp line of demarcation can be established, for there are numerous intermediaries between both kinds of solutions.

[1] Anorganische Fermente, loc. cit., pp. 10–12.

2. Limitation as to Suspensions

But little has been said of the characteristics which distinguish colloidal solutions from undoubted suspensions; a few words on this topic are therefore added.

In opposition it might be said that there is such a manifest difference between real suspensions, for instance, sediments of powdered substances like quartz, starch, metal dust, suspensions of bacteria, etc., and clear, colloidal solutions, that no words need be wasted on this subject. Nevertheless I do not regard it unnecessary to consider the matter, because here too there are intermediate forms which lead so gradually from one class to the other, that an observer, having in mind only the intermediate forms, is apt to miss the remarkable difference between the members of both groups.

(1) In the first place there is an enormous difference in size between the particles in hydrosols and those found in real suspensions. A glance at Plate III, Chapter XV, will make this more evident than words.

The following properties of colloids will serve in part to show the difference:

(2) Irreversible change of condition.

(3) Change of the total energy of the system by coagulation.

(4) Absorption of the subdivided substance by porous bodies, such as charcoal.

(5) The property of colloids to enter into reactions among themselves, which bear a deceptive resemblance to chemical reactions, etc.

To avoid possible misunderstanding it might right here be stated that most of these differences between hydrosols and suspensions are dependent upon the degree of sub-

division of the material, and they are therefore not very great if closely adjoining members of the series be compared; but they become enormous when we compare typical representatives of true suspensions with those of colloidal solutions. These differences justify the classification into colloidal solutions and suspensions long ago established by chemists, physiologists, and physicians.

Let us now consider the differences (2) and (3) above noted.

But little expenditure of mechanical energy is necessary to stir up the fine powder of a practically insoluble substance into a suspension. If this is allowed to stand, gravity separates the powder from the bulk of the fluid. The sediment can again be stirred up and again allowed to settle. This process can be repeated as often as desired, the powder remaining unchanged, except that the distances between the particles will be larger after stirring them up, and smaller when they have settled.

In the case of coarse suspensions, the addition of electrolytes does not appreciably change the above described process; this can readily be shown by allowing a suspension of potato starch or quartz whose particles measure 0.06 mm. and over to settle first in pure water and then in a dilute solution of table salt. Finer suspensions, such as the turbidity due to clay, are precipitated by the addition of electrolytes, just as are colloidal solutions, but even in this case, as we shall see, characteristic differences can be determined.

If the suspended powder is completely separated by desiccation from the water in which it was distributed, the original subdivision can be reproduced by stirring, provided that certain colloids which tend to cement together the individual particles are absent.

But if an attempt is made to separate a colloidal metal,

gold for instance, from the medium in which it is distributed (which can easily be done by evaporating the fluid or adding electrolytes), it undergoes an irreversible change of condition, or coagulates as we say. The metal thereby completely loses its capability of resuming its original condition of subdivision by shaking or stirring, and the coagulation involves profound changes in its relations to light waves, as evidenced by change of color, polarization, etc.[1]

Regarding these changes produced by coagulation, we understand with certainty only one, that is that numerous small submicroscopic [2] particles, which I will call α-particles, are combined into larger, but still submicroscopic particles (β-particles). Comparison with the flocculation of fine suspensions, carefully studied by many investigators,[3] has led to the conclusion that the submicroscopic β-gold particles are grouped together like the flocks in kaolin, clay, etc.; but in order to avoid unwarranted conclusions based upon analogy, see the relative sizes given in Plates III and IV, Chapter XV. To see the vast difference just imagine flocks made up of the clay particles or anthrax bacilli shown in Plate III, and compare them with imaginary flocks made up of gold particles which, though magnified 10,000 times, appear as tiny points. It will at once be seen that α-gold particles in such a "gold flock," must be much closer together than the kaolin particles in a clay flock, and that the attractive forces which we suppose to exist between the smallest

[1] The difference between suspensions and irreversible colloidal systems was known to Hardy, although not sharply characterized.

[2] For definition, see Chapter VI.

[3] See Barus and Schneider, Zeitschr. physik. Chem., Vol. VIII, p. 278, 1891; Quincke, Drude's Ann., Vol. VII, p. 59, 1902; Bodländer, Gött. Nachr. 1893.

particles of a substance (cohesion forces), will effect a much more powerful union of the α-particles than in ordinary flocks of coarser material.

But even without this exposition, just by the aid of rough experiments, we can easily establish the difference between the flocculation of fine clay particles, and the coagulation of colloidal metals.

As far back as 1870, Ch. Schlösing showed [1] that the turbidity due to clay could, after its precipitation by salts of calcium or magnesium, be once more suspended in water and again flocculated by the addition of salts.[2] On the contrary, coagulated colloidal gold cannot be brought into colloidal solution by stirring it up in pure water, even if all salt solution has been previously washed out. There results only a suspension of β-gold particles, which soon deposits its gold.

In order to change β-gold into α-gold we must make use of chemical or electrical energy, for instance solution in aqua regia and reduction of the gold chlorid to colloidal gold, or electric atomization by Bredig's method.

Finally coagulation involves change, considerable at times, in the total energy of the system, which can be directly determined by the calorimeter. Thus Prange (Chapter III) found that one gram of colloidal silver on precipitation by ammonium citrate, developed 250.98 to 126.73 calories, depending on whether a dilute or a concentrated solution was precipitated. Every gram-atom of silver accordingly liberates 27,100 to 13,700 calories. Even this does not yield the ordinary metallic condition. The conversion of the hydrogel into the metal (by means of H_2SO_4) sets free more heat, 60 calories per gram of silver, according to Prange.

[1] Ch. Schlösing, Compt. rend., Vol. LXX, p. 1345, 1870.

[2] Sometimes this flocculation is erroneously called coagulation.

Barus and Schneider, in commenting on Prange's observations, say:

"In his experiments on colloidal silver, Prange found that the transformation of the almost solid colloid into normal silver liberated about 60 calories. Prange attributes this to the change of colloidal into normal silver. But the liberation of heat can be explained in the following manner: Work is necessary to transform a quantity of silver, already finely subdivided (normal silver) into a considerably finer state of subdivision (colloid)—that is, heat is necessary. Reversing the process, the transformation of colloidal silver into the precipitate of normal silver (consisting of larger particles of the substance) liberates the heat again."

On this point I agree entirely with Barus and Schneider. The size of the coagulated silver particles, as figured by these authors, approximates the true value, and is rather too small than too large.

On the other hand the difference between the colloidal solution and suspension containing the same percentage of the same substance is evidence to me of a remarkable difference between the two kinds of subdivision. It is to be noted that the energy difference between suspended and colloidal silver is greater per gram-atom than that between the allotropic modifications of phosphorous, carbon, sulphur, etc.

Intermediate Forms between Suspensions and Colloidal Solutions. Between the coarse mechanical suspensions and colloidal solutions there are many intermediate forms. In general the finer a body is subdivided the more it assumes the properties of a colloid.

Even with potato and wheat starch we can readily see the influence of subdivision. While the settlement of the former is scarcely influenced at all by the addition of an

electrolyte, the finer particles of the latter exhibit a distinct flocculation and accelerated settlement upon the addition of table salt.

Turbidity due to clay, ultramarine, the much investigated mastic-turbidity, and others, form good examples of the intermediate forms between colloidal solutions and suspensions.

By pointing out the relations between fine suspensions and colloidal solutions, and thus establishing a new point of view, Ebell, Ostwald, Barus and Schneider, Spring, Lottermoser and von Meyer, and particularly Bredig, have rendered a great service which has already proved useful in leading the supporters as well as the opponents of this view to a series of experiments and the establishment of important facts.

Summary. Colloidal metal solutions are differentiated from true suspensions of pulverized substances, not only by the dissimilar subdivision of the solid body but also by the irreversible change of constitution invariably shown by colloidal solutions; and further by change of the total energy liberated upon the separation of the atomized substance from the medium. There are many intermediate forms between the two classes of subdivision, so that there is a continuous series, one leading to the other.

The colloidal metal solutions have been purposely considered, to establish the distinguishing characteristics between colloidal solutions or hydrosols and true suspensions, because they show a striking similarity to certain fine suspensions in their behavior with reagents. This similarity has led to the attempt on the part of some investigators to remove them from the group of colloidal solutions and classify them as suspensions. We must oppose such a conclusion, based as it is on one-sided

observation, because of the distinguishing characteristics before given. Real metal hydrosols rather tend to form a class of colloidal solutions, which is distinguished from the majority of the others, not by a lesser degree of subdivision but by the nature of the original substance.

We will take this up more fully later.

CHAPTER II

CLASSIFICATION OF HYDROSOLS ACCORDING TO TWO DIFFERENT POINTS OF VIEW[1]

ONE of the most important tasks of a nascent science appears to me to be the arrangement of the available facts upon one single basis.

If only an imperfect attempt in this direction can be made, it is because the point of view is so new, and the facts are so incompletely known. I consider it of importance, however, to direct the attention of investigators to this subject.

Just as geologists distinguish, according to the size of their constituent particles, between boulders, rubble, pebbles, gravel, sand, and dust, so too in dealing with more finely subdivided bodies, a classification based on the size of the particles will be of corresponding value.[2]

[1] The best classification of colloids yet suggested is that of Hardy (Zeitschr. f. physik. Chem., Vol. XXXIII, p. 326). Recently Müller (Zeitschr. f. anorg. Chem., 1903, Vol. XXXVI, p. 340) suggested a classification with which I cannot agree, for reasons that may in part be gathered from the following chapters. Nevertheless I fully agree with Müller that colloidal chemistry must establish a classification of hydrosols. Independently of Hardy, the changes of condition of colloids have been divided by Wolfgang Pauli (Arch. f. d. ges. Physiologie, 1899, Vol. LXXVIII, p. 315), into those easily and those with difficulty reversible.

[2] A classification of the various kinds of sand, pebbles, and dust, according to the size of their granules, has been attempted by Dr. Albert Atterberg, of Kolmar (Schwed. landw. Akad., 1903, and Chem. Ztg., 1905, Vol. XXIX, p. 195). The capillarity (the height in milli-

Pieces of like size have certain properties in common; for instance, sand and dust are carried by the wind, while cobble-stones and pebbles are unmoved; it makes no difference of what material the sand, dust, or pebbles consist. Sand will pass through a 10 mm. mesh sieve, but cobblestones and pebbles will not.

Weight has a noticeable effect on suspensions, producing the deposition of the suspended particles; and its influence can be traced down to particles as small as one tenth of a wave length of light. With particles smaller than 60 $\mu\mu$,[1] and even often with larger ones, its influence is masked by that of the electrical charge of the particles and by the influence of other kinds of energy. Furthermore in the case of much finer subdivisions, which we will take up later, the size of the particles immediately determines a whole series of properties. We would be anticipating if we discussed here the change of properties dependent upon the size of the particles. Part of the experimental

meters to which water will ascend in sand) as well as the permeability with respect to water, are intimately dependent upon the size of the granules, both of which facts have great significance in agriculture. Atterberg (a Swede) makes the following classification of the fragmental pieces:

	Diameter
Block (boulders)	2 m. to 20 cm.
Klapper (pebbles)	20 cm. to 2 cm.
Grus (gravel)	2 cm. to 2 mm.
Sand (sand)	2 mm. to 0.2 mm.
Mo (earth)	0.2 mm. to 0.02 mm.
Lättler (loam)	0.02 mm. to 0.002 mm.
Ler (clay)	smaller than 0.002 mm.

With each of these various sizes are associated definite physical properties. Loam shows great capillarity, but little permeability; sand 2 mm. in diameter has a capillarity of only 25 mm.; gravel and pebbles have no perceptible capillarity; earth (mo) allows water to soak through quickly. (Capillarity, 428–2000 mm.)

[1] 1 $\mu\mu$ = 1/1,000,000 mm.

section of this book deals with this subject. Polarization, the color of the particles in many cases, their behavior under the action of gravity and during filtration, the energy-content of the system, and the movement of the individual particles—all these vary with their increasing or diminishing size.

One change must be mentioned here. While suspensions of larger particles, for example, 1–10 μ, always possess a particularly inhomogeneous appearance,[1] fluids containing particles smaller than 20 $\mu\mu$ appear clear by ordinary daylight, even if the indices of refraction of the medium and subdivided substance are as different as those of water and metallic gold. While particles of the former kind can be easily and completely separated from the fluid *in which they float*, by filtration through filter paper, *the very actively moving* particles of the latter cannot by this means be separated from the fluid. It has been customary for chemists to designate as solutions,[2] subdivisions of such perfect homogeneity, that, like the latter class above

[1] It is here assumed that the particles and medium have different indices of refraction, as is generally the case.

[2] These solutions with particles of about 20 $\mu\mu$ and less are not without influence on light, although by ordinary daylight they appear clear and transparent. With the intense transverse illumination of direct sunlight their characteristic inhomogeneity is easily recognized by their characteristic scattering and polarization of light. Although this method has long been known to physicists, it was neglected by chemists; for the slight turbidity almost always present, even if visible without direct sunlight, was ascribed to contamination of the solution by larger suspended particles. Finally more recent investigations (Picton and Linder, Spring, Lobry de Bruyn, and others) have made evident the universality of this phenomenon, and shown that a large majority of colloidal and crystalloidal solutions are optically inhomogeneous But even this inhomogeneity, most conspicuous at 20 $\mu\mu$, becomes less and less, and almost or entirely vanishes with all substances in the neighborhood of the molecular dimensions. (See Introduction and Chapter IX.)

described, they are clear, transparent, and do not settle. Subdivisions of the former class are, on the other hand, considered as sediments or suspensions. Accordingly, if we arbitrarily omit the intermediate members (between 1000 and 20 $\mu\mu$) we can differentiate according to the size of the particles, two sharply defined groups of subdivisions—coarse mechanical suspensions with particles from about 1 μ and over, and apparently homogeneous solutions with particles of 20 $\mu\mu$ and less. Between these two classes of subdivisions come the transition forms which, according to their properties, are classed sometimes as colloidal solutions, sometimes as fine suspensions.

These remarks suffice to show the importance of a classification based on the size of the particles.

Before taking this up, we must first consider the classification established by Graham, and also that of Hardy. Graham divides homogeneous looking subdivisions, that is solutions, according to their greater or lesser diffusibility, into solutions of crystalloids and colloids. This classification of Graham is an exceptionally happy one, for although it establishes no sharp boundary between the two groups,[1] it brings into prominence a series of contrasts between the members of both classes of solutions.

In general, crystalloidal solutions are regarded as the complete subdivision of the substance, and colloidal solutions as the less complete. But it cannot reasonably be held that all crystalloidal solutions without exception possess a higher degree of homogeneity than colloidal solutions. In the following chapters we will learn of one case of colloidal solution where the subdivision is evidently carried as far as in the case of a crystalloid solution, and is probably even more complete.

[1] Graham himself knew of the transition forms between crystalloid and colloid solutions.

(Compare Chapters IX, XVII, and XVIII (*b*).

On the other hand, coarse subdivisions, such for example as are formed by washing out sulphids, and which pass through filter paper, would be classed as colloidal solutions, and it was just in the case of such subdivisions that the heterogeneity of hydrosols was first dicovered. Regarding these relative proportions, reference should be made to the diagram, Plate I, which is based upon the size of the particles. If the subdivisions are arranged in successive order according to the size of their particles, beginning above, having the largest at the top and the smallest at the bottom, the relative sizes may then be seen at a glance.

Several investigators have expressed the opinion that those colloidal solutions (such as the metal hydrosols) which, upon the addition of electrolytes, act as do suspended clay particles, should be considered as suspensions, and not as colloidal solutions at all. From this it might be assumed that, in the diagram, the metal hydrosols would lie next to or be included in with the suspensions; while those hydrosols which are not precipitated by traces of electrolytes would be nearer the solutions—that is, they would be in a finer state of subdivision. Such is not the case, however. Another classification than the preceding, one which, *up to a certain point*, is independent of the size of the particles, would be made by studying the effect of the addition of electrolytes, and of changes of temperature on the subdivisions.

Such a classification was first successfully introduced by Hardy. He divided the colloids into those reversible and those irreversible, according as the change from sol to gel could or could not be made retrogressive by reversing the conditions of its production. The conditions studied by

Hardy[1] as causing hydrogel formation were chiefly changes of temperature and the addition of electrolytes. But difficulties arise on attempting a classification of colloids in general, according to Hardy's method. Only in individual cases do ordinary changes of temperature lead to the formation of gels, as in the case of gelatin solutions which were closely studied by Hardy. Extreme changes of temperature (complete freezing, for instance), almost always lead to gel formation, but they sometimes cause irreversible change of constitution in the case of colloids classed by Hardy as reversible (gelatin, for example).

If the changes produced by the addition of electrolytes are studied, it will be found that a certain hydrosol undergoes sometimes a reversible and sometimes an irreversible change of condition, according to the nature of the electrolyte added, so that it may appear doubtful to which class the hydrosol belongs.[2] Thus the hydrosol of stannic acid is converted into a hydrogel by the addition of the slightest trace of most electrolytes. However, while acids and many salts give a hydrogel which remains insoluble after the elimination of the precipitant,[3] other precipitants for example table salt or caustic alkalis, yield precipitates which redissolve in water upon the elimination of the reagent.

In order therefore to make practical a classification along the lines laid down by Hardy, it is necessary to consider only such influences on the hydrosol as always lead to formation of gels or of solid colloids, and which, as far

[1] Hardy, Zeitschr. f. physik. Chem., 1900, Vol. XXXIII, pp. 326 and 385.

[2] Pauli first referred to this; loc. cit.

[3] Lottermoser calls water-soluble colloids solid hydrosols. According to Hardy, however, we must regard jellies and solid colloids as hydrogels, even if they are soluble in water. The word hydrogel is used here in this sense.

as possible, are independent of chance or outside influences, as well as of the personal equation.

Evaporation is a method of treatment which in every case leads to the formation of a gel or of a solid residue. It is sufficient for our purpose to class as reversible those colloids whose solutions leave a residue soluble in water, when desiccated at ordinary temperatures;[1] and to consider as irreversible those colloids which, under the same circumstances, yield a residue insoluble in water.

According to this classification, dextrin, gum arabic, most albumens, molybdic oxid, molybdic acid, etc., are reversible colloids, while, on the other hand, stannic acid and many other colloidal oxids and sulphids, as well as the pure colloidal metals, etc., are irreversible colloids.

While the former are frequently insensitive to the addition of electrolytes, the latter for the most part are extremely sensitive, and are easily coagulated by the slightest addition of electrolytes. If solutions of reversible are added to those of the irreversible colloids, the latter may become reversible, in which case they are often protected against precipitation by salts (Schutzwirkung). Frequently a very small addition of a reversible colloid is sufficient to produce these effects in a striking manner. Carey Lea's colloidal silver, which can never be prepared free from foreign colloids, commercial argentum Credé, collargol, Paal's colloidal metals, Möhlau's colloidal indigo,

[1] As will be seen, Hardy's basis of classification is adhered to; but instead of numerous conditions which lead to gel formation, here only one is taken into consideration. Evaporating the hydrosol is a very efficient means of causing gel formation; on increasing concentration many colloids are transformed into insoluble hydrogels, even though wet, while others lose their solubility on further evaporation. The reversible hydrosols, on the other hand, even after evaporation to dryness, retain the property of distributing themselves in water in their original condition.

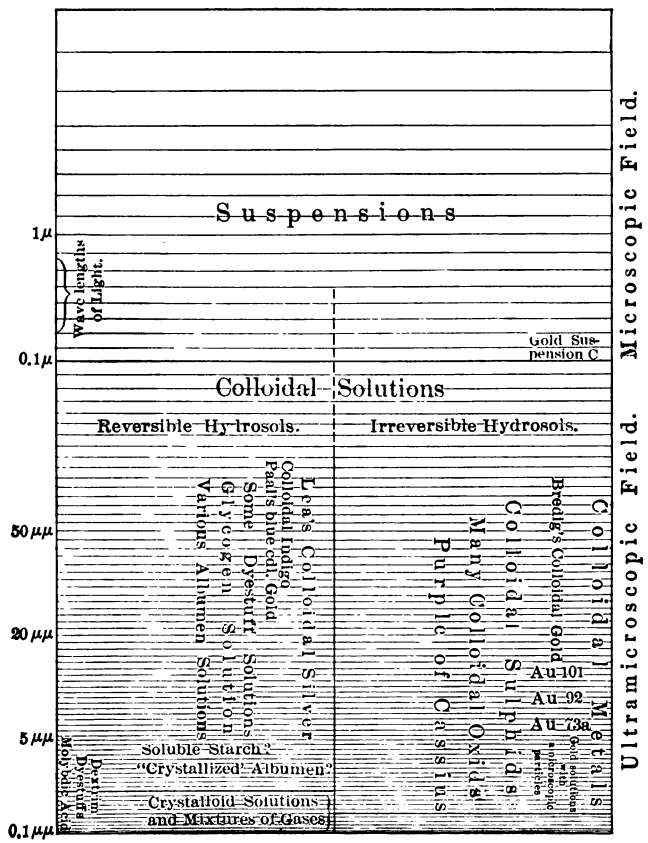
all owe their solubility in water to the presence of protective colloids.[1]

The accompanying diagram, Plate I, shows how colloidal solutions and suspensions may be grouped according to the size of their particles. Above, in the microscopic field and below, even extending into the ultramicroscopic field, are to be found *true suspensions*, whose sphere extends much further up than is shown in the diagram.

Colloidal solutions or hydrosols all contain ultramicroscopic particles. No sharp line of demarcation can be drawn between suspensions and colloidal solutions; their spheres mutually invade each other; that of the *hydrosols* being here extended as far upwards as possible, to include everything which has formerly been classed as a colloidal solution. Several typical hydrosols are mentioned in the table. A perpendicular through the cross-hatching lines divides the whole area into two sections; on the right are the irreversible, on the left the reversible colloids. This division simplifies the diagram. It will be seen that on the right are those hydrosols which are distinguished by especial sensitiveness to electrolytes. This does not mean, however, that colloidal metals (and sulphids, etc.), more nearly approach suspensions than do reversible

[1] By the classification here followed two groups will be distinguished, whose typical representatives differ from each other in several important particulars. As everywhere in nature there are also transitions here; nevertheless a sharp separation could be made if the conditions upon desiccation, such as temperature, moisture-content of the gas-phase, etc., are predetermined. An advantage of this classification is that outside influences which might act chemically upon the colloid, such as increase of temperature, chemical action of foreign electrolytes, etc., are as far as possible avoided. On the other hand, possible chemical changes upon desiccation of the colloid, are left out of consideration, for it is almost impossible to determine such changes satisfactorily and to separate them clearly from the physical changes that always occur.

PLATE I



Classification of Colloidal Solutions

according to the size of the particles contained in them and according to their behavior upon dessication.

[*To face page* 26.]

hydrosols (glycogen, albumen, etc.), as has often been maintained, but that they tend of themselves to assume the stable form—that is, the solid compact form of the substance (metal, sulphid, or oxid). This tendency is realized upon evaporation, as well as upon the addition of electrolytes. Such addition hastens the process, which in most cases takes place of itself.[1] The very finest subdivisions of metals are sometimes the most sensitive and coagulate very readily.

It must, however, be noted that the behavior of hydrosols upon evaporation cannot always be foretold from their reaction with electrolytes. Most reversible colloids—for instance, molybdic acid, tungstic acid, gum, albumen, gelatin—are not sensitive to small additions of electrolytes. On such addition either they are not precipitated or else they undergo a reversible precipitation, which, upon elimination of the precipitant, can be made retrogressive. (On this subject see W. Pauli.[2]) But there are also colloids, reversible according to the above classification, which are extremely sensitive to the addition of electrolytes of every kind, Graham's caramel, for example. (Chapter III). In this case the specific influence of the subdivided substance or of its constituents, is distinctly changed.

In the table sulphids, oxids, etc., are placed with the colloidal metals, while glycogen, albumen, etc., are grouped with the reversible colloids. The names written vertically indicate that these fluids may contain particles of the most diverse sizes, but not, however, that any one fluid must necessarily contain all sizes.

Linder and Picton have already differentiated various

[1] Electrolytes are not, however, to be here considered as catalysers. (See Chapter XVIII, also W. Pauli, Ergebnisse der Physiologie, 1904, p. 157).

[2] W. Pauli, Pflügers Archiv., 1899, Vol. LXXVIII, p. 315.

kinds of arsenic sulphid according to their method of preparation, which they called arsenic sulphid α, β, γ, and δ, and they have shown that the fluid $As_2S_3\alpha$ contains the largest, while $As_2S_3\delta$ contains the smallest particles.[1]

Ultramicroscopy enables us to fix the approximate sizes when the particles can be rendered visible, and when these are known, the diagram, which is only outlined here, can be then partially filled in. As an illustration several colloidal gold solutions described in detail in the experimental section of this book (see Chapter IX), are arranged according to the sizes of their particles.

At the bottom following the fluids Au_{73a}, Au_{92}, etc., are gold solutions with amicroscopic particles, which conclude the series beginning with Bredig's colloidal gold, having particles from 20 to 80 $\mu\mu$ in size. Above is the gold suspension *c* which deposits its gold; above this should be placed the well-known suspensions of gold, obtained by precipitating a solution of gold chlorid with $FeSO_4$ or oxalic acid.

By way of further explanation of the diagram, it might be said that the individual particles of most colloidal inorganic oxids cannot be seen, for they, as well as most organic colloids, are not so easily rendered visible as are colloidal metals, and therefore I have formed no idea as to the size of their particles. Colloidal stannic acid contains, according to its method of preparation, submicrons [2] or amicrons.[2] The same is the case with the purple of Cassius and colloidal silicic acid.

Among the reversible colloids are included: Möhlau's

[1] Picton and Linder (loc. cit. in Chapter III) based their conclusions regarding the difference of the sizes of the particles, upon the behavior of the fluids when filtering through porcelain and upon diffusion experiments.

[2] Definition, see Chapter VI.

colloidal indigo and Paal's blue colloidal gold, which contain quite large copper-red particles [1]; Lea's colloidal silver with particles of various size; and further, on the basis of the work of Raehlmann, Much, Römer and Siebert, Biltz and Gatin-Gruzewska, as well as Michaelis (Chapter XX), glycogen, several kinds of albumen, dyes with particles which are ultramicroscopically visible, but whose size is not yet determined.

Lower down are soluble starch and crystallized albumen with question marks attached, because, although they show a light-cone (lichtkegel), their individual particles cannot be distinguished, but probably are about 5 $\mu\mu$. Finally, at the side are dextrin, many dyes such as Congo red, etc., and molybdic acid, etc., which from their general properties are all to be regarded as intermediate between crystalloidal and colloidal solutions, or else, like soluble starch, as crystalloid solutions with high molecular weight. If a 3 per cent solution of soluble starch is allowed to stand, in course of time particles are formed in it, which may grow up to 100 $\mu\mu$ (see Chapter XXI).

At the very bottom of the reversible colloids I have placed the crystalloidal solutions and gas mixtures, not because the sizes of their particles can as yet be demonstrated experimentally by any method independent of theory, but just for the sake of completeness. In the present state of our knowledge, the hypothetical molecules of the crystalloids will serve quite well and be unobjectionable for the purpose of this table.

[1] The respective sizes of these particles are not yet determined, their appropriate place in the table is therefore still uncertain.

CHAPTER III

HISTORY OF THE IRREVERSIBLE COLLOIDS

1. Graham's Investigations

SINCE the time when chemists commenced the examination and description of animal and vegetable materials, colloidal substances have been investigated and described, and that in much greater detail in the older than in the modern text books of organic chemistry. In addition, many isolated observations on inorganic colloids have been made and recorded in recent years.

To Thomas Graham is due the credit of having recognized and described in detail the similarity in the various phenomena, and of having first proposed a classification that gave an insight into the essential differences between the two separate classes of solutions. Here, as in many other instances, progress followed the discovery of a new method. While working on diffusion experiments, Graham found that those substances which easily crystallize from their solutions, would readily diffuse through jelly-like membranes, while on the contrary, amorphous substances either lacked this property or possessed it to only a very limited degree. Membranes of parchment paper are particularly suitable for this work. By their aid Graham could not only easily separate crystalloids from colloids, but could also prepare a large number of the latter in a sufficient state of purity. He also introduced the expressions now in general use; colloid, crystalloid, hydrogel,

hydrosol, etc. Graham's work must therefore be discussed in detail, especially as it is not well enough known.[1] A considerable part will be given in Graham's own words:[2]

Liquid Diffusion Applied to Analysis

By THOMAS GRAHAM, F.R.S., Master of the Mint

(Received May 8, Read June 13, 1861)

"The property of volatility, possessed in various degrees by so many substances, affords invaluable means of separation, as is seen in the ever-recurring processes of evaporation and distillation. So similar in character to volatility is the diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise from it. The range also in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapor tensions. Thus hydrate of potash may be said to possess double the velocity of diffusion of sulphate of potash, and sulphate of potash again double the velocity of sugar, alcohol, and sulphate of magnesia. But the substances named, belong all, as regards diffusion, to the more "vola-

[1] In contradistinction to this fundamental work, other publications regarding irreversible hydrosols are rather briefly treated here. In the quotations there is no claim to completeness; much important work is passed over, the main object being to direct attention to certain points. The complete literature of the subject, in so far as not here given, can be found in A. Lottermoser, "Uber anoganische Kolloide," Stuttgart, 1901, and A. Müller, "Die Bibliographie der Kolloide" (Zeitschr. f. anorg. Chemie, 1904, Vol. XXXIX, p. 121). Work concerning the theory of colloids is referred to only in so far as germane. See also Bredig, "Anorganische Fermente"; A. Müller, "Die Theorie der Kolloide," Leipzig and Vienna, 1903; Billitzer (Zeitschr. f. physikal. Chemie, 1905, Vol. LI, pp. 129–166).

[2] Thomas Graham, Philosophical Transactions of the Royal Society of London, 1861, Vol. 151, pp. 183–224. (Also Liebig's Annalen, 1862, Vol. CXXI, pp. 1–77).

tile" class. The comparatively "fixed" class, as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which are slow in the extreme. Among the latter are hydrated silicic acid, hydrated alumina, and other metallic peroxids of the aluminous class, when they exist in the soluble form; with starch, dextrin, and the gums, caramel, tannin, albumen, gelatin, vegetable, and animal extractive matters. Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation with the chemical indifference referred to, appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatin appears to be its type, it is proposed to designate substances of the class as *colloids*, and to speak of their peculiar form of aggregation as the *colloidal condition of matter*. Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as *crystalloids*. The distinction is no doubt one of intimate molecular constitution.

"Although chemically inert in the ordinary sense, colloids possess a compensating activity of their own, arising out of their physical properties. While the rigidity of the crystalline tructure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in such colloids as can

exist at a high temperature. Hence a wide sensibility on the part of colloids to external agents. Another and eminently characteristic quality of colloids, is their mutability. Their existence is a continued metastasis. A colloid may be compared in this respect to water, while existing liquid at a temperature under its usual freezing-point, or to a supersaturated saline solution. Fluid colloids appear to have always a *pectous* modification; and they often pass under the slightest influences from the first into the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble at last. Nor does the change of this colloid appear to stop at that point. For the mineral forms of silicic acid, deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition. (H. Rose). The colloidal is, in fact, a dynamical state of matter; the crystalloidal being the statical condition. The colloid possesses Energia. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element), may the characteristic protraction of chemico-organic changes also be referred." [1] (Pp. 183–184).

[1] Some of Graham's general statements are at the present day open to criticism. Thus it is not quite right to state that colloids are incapable of passing over into the crystalline condition. Not all colloids give jellies; van Bemmelen has also shown that in the case of the hydrogels there is hardly a real chemical hydrate. Chemical inactivity and the slowness of reaction often referred to by Graham are not always characteristic of colloids. Objection might also be made to many other statements, but it should, however, be remembered that

Graham then describes the simple jar diffusion experiment and remarks that separation by diffusion is due to the property possessed by crystalloids of easily passing through jelly-like masses of mucus, starch, gelose, etc., which offer great resistance to or completely prevent the passage of colloids. For instance, with a mixture of sugar and gum arabic, thin French letter paper will practically allow only the former to pass through. This separation is analogous to that of carbonic acid and hydrogen by a thin film of water. He then continues:

"It may perhaps be allowed to me to apply the convenient term *dialysis* to the method of separation by diffusion through a septum of gelatinous matter. The most suitable of all substances for the dialytic septum appears to be the commercial material known as vegetable parchment, or parchment-paper, which was first produced by M. Gaine, and is now successfully manufactured by Messrs. De la Rue." (P. 186.)

The experiments made by the jar-diffusion method, the importance of which in physical chemistry has long been known, are described in detail on pages 186–199. Graham then takes up dialysis proper, describes the dialyzer and discusses the precautionary measures to be taken in carrying out the process. (Pp. 199–204.)

Preparation of Colloid Substances by Dialysis

"The purification of many colloid substances may be effected with great advantage by placing them on the dialyzer. Accompanying crystalloids are eliminated, and the colloid is left behind in a state of purity.[1] The purifi-

Graham was the first to recognize the similarity underlying the great variety of colloids, and also that his papers were written more than forty years ago.

[1] This should not be regarded as meaning that by dialysis a com-

cation of soluble colloids can rarely be effected by any other known means, and dialysis is evidently the appropriate mode of preparing such substances free from crystalloids.

"*Soluble Silicic Acid.* A solution of silica is obtained by pouring silicate of soda into diluted hydrochloric acid, the acid being maintained in large excess. But in addition to hydrochloric acid, such a solution contains chlorid of sodium, a salt which causes the silica to gelatinize when the solution is heated, and otherwise modifies its properties. Now such soluble silica, placed for twenty-four hours in a dialyzer of parchment-paper, to the usual depth of 10 millimetres, was found to lose in that time 5 per cent of its silicic acid and 86 per cent of its hydrochloric acid. After four days on the dialyser, the liquid ceased to be disturbed by nitrate of silver. All the chlorids were gone, with no further loss of silica. In another experiment 112 grams of silicate of soda, 67.2 grams of dry hydrochloric acid, and 1000 cc. of water were brought together, and the solution placed upon a hoop dialyzer, 10 inches in diameter. After four days the solution had increased to 1235 cc, by the action of osmose, colloid bodies being generally highly osmotic. The solution now gave no precipitate with nitrate of silver, and contained 60.5 grams of silica, 6.7 grams of that substance having been lost. The solution contained 4.9 per cent of silicic acid.[1]

plete elimination of crystalloids is always secured, although the purification is so perfect that the impurities often fall below the limit of analytical determination (Zs).

[1] Jordis and Kanter (Zeitschr. f. anorg. Chemie., 1903, Vol. XXXV, p. 18), have found, contrary to Graham, that in the dialysis of colloidal silicic acid, the chlorin reaction of the contents of the dialyser taken from one to three weeks to disappear. Variations in the quality of the parchment membranes and in the conditions of the dialysis influence

"The pure solution of silicic acid so obtained may be boiled in a flask and considerably concentrated, without change; but when heated in an open vessel a ring of insoluble silica is apt to form round the margin of the liquid, and soon causes the whole to gelatinize. The pure solution of hydrated silicic acid is limpid and colorless, and not in the least degree viscous, even with 14 per cent of silicic acid. The solution is the more durable the longer it has been dialyzed and the purer it is. But this solution is not easily preserved beyond a few days, unless considerably diluted. It soon appears slightly opalescent, and after a time the whole becomes pectous somewhat rapidly, forming a solid jelly, transparent and colorless, or slightly opalescent and no longer soluble in water. This jelly undergoes a contraction after a few days, even in a close vessel, and pure water separates from it. The coagulation of the silicic acid is effected in a few minutes by a solution containing 1/10,000th part of any alkaline or earthy carbonate, but not by caustic ammonia, nor by neutral or acid salts. Sulphuric, nitric, and acetic acids do not coagulate silicic acid, but a few bubbles of carbonic acid passed through the solution produce that effect after the lapse of a certain time. Alcohol and sugar, in large quantity even, do not act as precipitants; but neither do they protect silicic acid from the action of alkaline carbonates, nor from the effect of time in pectizing the fluid colloid. Hydrochloric acid gives stability to the solution; so does a small addition of caustic potash or soda.

"This pure water-glass is precipitated on the surface

its course in a high degree, and perhaps this is the cause of their lack of agreement with Graham. Neither in the English nor German text of Graham's work does it appear that he tested for chlorin only the exterior water and not the dialyser contents, as Jordis and Kanter seem to assume.

of a calcareous stone without penetrating, apparently from the coagulating action of soluble lime-salts. The hydrated silicic acid then forms a varnish, which is apt to scale off on drying. The solution of hydrated silicic acid has an acid reaction somewhat greater than that of carbonic acid. It appears to be really tasteless (like most colloids), although it occasions a disagreeable persistent sensation in the mouth after a time, probably from precipitation.

"Soluble hydrated silicic acid, when dried in the air-pump receiver, at 15°, formed a transparent glassy mass of great luster, which was no longer soluble in water. It retained 21.99 per cent of water after being kept two days over sulphuric acid.

"The colloidal solution of silicic acid is precipitated by certain other soluble colloids, such as gelatin, alumina, and peroxid of iron, but not by gum nor caramel. As hydrated silicic acid, after once gelatinizing, cannot be made soluble again by either water or acids, it appears necessary to admit the existence of two allotropic modifications of that substance, namely, soluble hydrated silicic acid, and insoluble hydrated silicic acid, the fluid and pectous forms of this colloid." (Pp. 204–205).

Ordinary sodium silicate is not a colloid; it diffuses through membranes. Colloidal silicic acid has an acid reaction which can be neutralized by alkalis.[1]

"The acid reaction of 100 parts of soluble silicic acid is neutralized by 1.85 part of oxid of potassium, and by corresponding proportions of soda and ammonia. The *colli*-silicates or *co*-silicates thus formed are soluble and more durable than fluid silicic acid, but they are pectized by carbonic acid or by an alkaline carbonate, after standing for a few minutes. The co-silicate of potash forms a

[1] See Jordis (Zeitschr. f. Electrochemie, 1902, No. 36.)

transparent hydrated film on drying *in vacuo*, which is not decomposed by water, and appears to require about ten thousand parts of water to dissolve it. The silicate of soda which Forchhammer obtained by boiling freshly precipitated silicic acid with carbonate of soda, and collecting the precipitate which falls on cooling, contains 2.74 per cent of soda, and is represented by $NaO + 36SiO_2$ (Gmelin). This silicate is probably a co-silicate of soda in the pectous condition. Soluble silicic acid produces a gelatinous precipitate in lime-water, containing six per cent and upwards of the basic earth. This and the other insoluble earthy co-silicates appear not to be easily obtained in a definite state. They gave out a more basic silicate to water on washing. The composition of these salts and that also of the co-silicate of gelatin, were found to vary according as the mode of preparation was modified. When a solution of gelatin was poured into silicic acid in excess, the co-silicate of gelatin formed gave, upon analysis, 100 silicic acid with 56 gelatin, or a little more than half the gelatin stated above as found in that compound prepared with the mode of mixing the solutions reversed. The gallo-tannate of gelatin is known to offer the same variability in composition." (P. 206).

"*Soluble Alumina.* We are indebted to Mr. Walter Crum for the interesting discovery that alumina may be held in solution by water alone in the absence of any acid. But two soluble modifications of alumina appear to exist, alumina and metalumina. The latter is Mr. Crum's substance.

"A solution of the neutral chlorid of aluminium (Al_2Cl_3), placed on the dialyzer, appears to diffuse away without decomposition. But when an excess of hydrated alumina is previously dissolved in the chlorid, the latter salt is found to escape by diffusion in a gradual manner, and the

hydrated alumina, retaining little or no acid, to remain behind in a soluble state. A solution of alumina in chlorid of aluminium, consisting at first of 52 parts of alumina to 48 of hydrochloric acid after a dialysis of six days, contained 66.5 per cent of alumina; after eleven days 76.5 per cent; after seventeen days 92.4 per cent; and after twenty-five days the alumina appeared to be as nearly as possible free from acid, as traces only of hydrochloric acid were indicated by an acid solution of nitrate of silver. But in such experiments the alumina often pectizes in the dialyzer before the hydrochloric acid has entirely escaped.

"Acetate of alumina with an excess of alumina gave similar results. The alumina remained fluid in the dialyzer for twenty-one days, and when it pectized was found to retain 3.4 per cent of acetic acid, which is in the proportion of one equivalent of acid to 28.2 equivalents of alumina.

"Soluble alumina is one of the most unstable of substances, a circumstance which fully accounts for the difficulty of preparing it in a state of purity. It is coagulated or pectized by portions, so minute as to be scarcely appreciable, of sulphate of potash and, I believe, by all other salts; and also by ammonia. A solution containing two or three per cent of alumina was coagulated by a few drops of well-water, and could not be transferred from one glass to another, unless the glass was repeatedly washed out by distilled water, without gelatinizing. Acids in small quantity also cause coagulation; but the precipitated alumina readily dissolves in an excess of the acid. The colloids gum and caramel also act as precipitants.

"This alumina is a mordant, and possesses indeed all the properties of the base of alum and the ordinary aluminous salts. A solution containing one half per cent of alumina may be boiled without gelatinizing, but when concentrated to half its bulk it suddenly coagulated.

Soluble alumina gelatinizes when placed upon red litmus paper and forms a faint blue ring about the drop, showing a feeble alkaline reaction. Soluble alumina is not precipitated by alcohol nor by sugar. No pure solution of alumina, although dilute, remained fluid for more than a few days.

"Like hydrated silicic acid, then, the colloid alumina may exist either fluid or pectous, or it has a soluble and insoluble form, the latter being the gelatinous alumina as precipitated by bases. It is evident that the extraordinary coagulating action of salts upon hydrated alumina must prevent the latter substance from ever appearing in a soluble state when liberated from combination by means of a base." (P. 207.)

"Soluble metalumina" can be produced, according to Crum's method, by boiling off the acetic acid from a solution of aluminium acetate, or according to Graham by dialyzing a solution of aluminium acetate altered by prolonged boiling. After six days the contents of the dialyzer still contains some acetic acid.

"The alumina exists in an allotropic condition, being no longer a mordant; and forming, when precipitated, a jelly that is not dissolved by an excess of acid. Metalumina resembles alumina in being coagulated by minute proportions of acids, bases, and of most salts. Mr. Crum found the solution of metalumina to require larger quantities of acetates, nitrates, and chlorids to produce coagulation than of the former substances. The solution of metalumina is tasteless, and entirely neutral to test-paper, according to my own observation.

"Like alumina, the present colloid has therefore a fluid and a pectous form, the liquid soluble metalumina, and the gelatinous insoluble metalumina." (P. 208.)

Graham then describes soluble ferric oxid and sesqui-

oxid, which are analogous to the corresponding aluminium colloids. The hydrosol of copper ferrocyanid is formed by mixing very dilute solutions of potassium ferrocyanid with copper sulphate (1:3000) and then dialyzing. Precipitated copper ferrocyanid is insoluble in potassium oxalate and oxalic acid, but is soluble in a quarter of its weight of neutral ammonium oxalate. A solution containing 3–4 per cent of copper ferrocyanid is dark red-brown in color, transparent to transmitted light, but cloudy to reflected light. Iron sesquioxid has the same appearance. On dialysis a little ammonium salt is strongly retained.

The solutions of copper ferrocyanid can be heated, but are easily made pectous by foreign substances, such as nitric, hydrochloric, or sulphuric acid (and also after gentle heating with oxalic and tartaric acid). Acetic acid does not have this effect. Metallic salts coagulate the solution. The colloidal solution of Prussian blue is made pectous by zinc sulphate, etc., but requires a large quantity of alkali salts for precipitation. Graham further describes soluble compounds of sugar with copper oxid, iron oxid, uranium oxid, and of sugar with lime. The latter upon heating forms a solid coagulum. The solution of copper tartarate in alkali is also colloidal. (Pp. 208–212.)

Soluble chromium oxid (p. 212) is produced similarly to soluble alumina; after thirty-eight days the solution in the dialyzer was partly gelatinous and contained 1.5 parts acid to 98.5 oxid or one equivalent of acid to 31.2 equivalents of chromium oxid. Traces of salts make it gelatinous, and then it is insoluble even in hot water.

"It appears, then, that the hydrated peroxids of the aluminous type, when free, are colloid bodies; that two species of each of these hydrated oxids exist, of which alumina and metalumina are the types; one derived from

an unchanged salt, and the other from the heated acetate of the base; further, that each of these species has two forms, one soluble and the other insoluble or coagulated. This last species of duality should be well distinguished from the preceding allotropic variability of the same peroxid. The possession of a soluble and an insoluble (fluid and pectous) modification is not confined to hydrated silicic acid and the aluminous oxids, but appears to be very general, if not universal, among colloid substances. The double form is typified in the fibrin of blood." (Pp. 212, 213.)

The ammoniacal solutions of copper and zinc oxids diffuse through a colloidal septum and are therefore not to be considered colloids.

Dialysis of organic colloid substances (pp. 213–217). Tannic acid passes through parchment paper about 200 times slower than sodium chlorid; gum arabic 400 times slower.

"The separation of colloids from crystalloids by dialysis is, in consequence, generally more complete than might be expected from the relative diffusibility of the two classes of substances." (P. 214.)

Vegetable gum, according to Fremy, is a gummate of lime, and after the addition of HCl, can be freed from lime by dialysis. One hundred parts of the remaining gummic acid was neutralized by 2.85 parts of potash. This quantity of potash is about equivalent to the lime originally present in the gum. The gummic acid, if dried at 100°, becomes insoluble in water. Gummic acid and glue give oily drops, which upon standing yield a colorless jelly, which becomes fluid at as low a temperature as 25° C.

Dextrin is colloidal, but slowly diffuses through animal mucus.

Caramel. Crude caramel, produced by heating raw sugar to 210–220°, when dialyzed allows a colored substance to pass through, while the substance richest in carbon remains behind. A ten per cent solution of this substance is gum-like and forms a weak jelly completely soluble in water. On evaporation in a vacuum, it dries to a black, shining mass, which still contains water and is tough and elastic. When thoroughly dry it can be heated to 120° and still remains completely soluble. If, however, the first solution is evaporated to dryness on the water-bath, it becomes insoluble. Soluble and insoluble caramel have the same constitution, represented by the empirical formula, $C_{24}H_{15}O_{15}$. Liquid caramel is quite tasteless, neutral in reaction, and is extremely sensitive to crystalloid reagents. Traces of mineral acids, alkali salts, and alcohol make it pectous; the precipitated caramel yields a brownish-black powdery substance insoluble in hot or cold water. "The presence of sugar and of the intermediate brown substances protects the liquid caramel in a remarkable degree from the action of crystalloids and accounts for the preceding properties not being observed in crude caramel."[1] Pectous caramel is easily rendered soluble again by dilute potash, in which it becomes gelatinous and then dissolves on heating. By acetic acid and dialysis, the potash can be removed once more, and pure, soluble caramel remains in the dialyzer. Caramel is 600 times less dialyzable than sodium chlorid and 200 times less than sugar. Graham refers to the analogy between caramel and anthracite coal: "Caramelization

[1] This is the first example of a protective action, recognized as such, and it is worthy of remark that substances capable of diffusion produce the same effect. I should here state that caramel acts similarly to colloidal gold, from which it differs, among other points, in the water-solubility of its dry residue (Zs).

appears the first step in that direction—the beginning of a colloidal transformation to be consummated in the slow lapse of geological ages." (P. 216.)

Albumen. Acetic acid was added to a solution of egg albumen, and the solution dialyzed; entirely ash-free albumen remained behind, which had a weak acid reaction. Pure albumen prepared according to Wurtz's method is 1000 times less dialyzable than sodium chlorid; if to it is added $\frac{1}{10}$ its weight of sodium hydrate, the latter alone will dialyze from the solution; and its separation from the albumen is complete. A film of albumen coagulated by heat is totally impermeable to albumen solution.

Neither gelatinized starch, nor an aqueous solution of animal gelatin, nor meat extract, diffuses through colloid septa.

Graham thereafter describes the well-known separation of arsenious acid from colloidal fluids by dialysis. (Pp. 217–219.)

"**Colloidal Condition of Matter.** I may be allowed to advert again to the radical distinction assumed in this paper to exist between colloids and crystalloids in their intimate molecular constitution. Every physical and chemical property is characteristically modified in each class. They appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and the material of an organized mass.

"The colloidal character is not obliterated by liquefaction, and is therefore more than a modification of the physical condition of solids. Some colloids are soluble in water, as gelatin and gum-arabic; and some are insoluble, like gum-tragacanth. Some colloids, again, form solid

compounds with water, as gelatin and gum-tragacanth, while others, like tannin, do not. In such points the colloids exhibit as great a diversity of property as the crystalloids. A certain parallelism is maintained between the two classes, notwithstanding their differences.

"The phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The process becomes slow; time, indeed, appearing essential to all colloidal changes. The change of temperature, usually occuring in the act of solution, becomes barely perceptible. The liquid is always sensibly gummy or viscous when concentrated. The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced and precipitated by the addition to their solution of any substance from the other class. Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa, are the most serviceable in distinguishing them from crystalloids. Colloids have feeble chemical reactions, but they exhibit at the same time a very general sensibility to liquid reagents, as has already been explained.

"While soluble crystalloids are always highly sapid, soluble colloids are singularly insipid. It may be questioned whether a colloid, when tasted, ever reaches the sentient extremities of the nerves of the palate, as the latter are probably protected by a colloidal membrane, impermeable to soluble substances of the same physical constitution. (P. 220.)

"A tendency to spontaneous change, which is observed occasionally in crystalloids, appears to be general in the other class. The fluid colloid becomes pectous and insoluble by contact with certain other substances, with-

out combining with these substances, and often under the influence of time alone. The pectizing substance appears to hasten merely an impending change. Even while fluid a colloid may alter sensibly, from colorless becoming opalescent; and while pectous the degree of hydration may become reduced from internal change. The gradual progress of alteration in the colloid effected by the agency of time, is an investigation yet to be entered upon.

"The equivalent of a colloid appears to be always high, although the ratio between the elements of the substance may be simple. Gummic acid, for instance, may be represented by $C_{12}H_{11}O_{11}$, but judging from the small proportions of lime and potash which suffice to neutralize this acid, the true numbers of its formula must be several times greater. It is difficult to avoid associating the inertness of colloids with their high equivalents, particularly where the high number appears to be attained by the repetition of a smaller number. The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule.

"With silicic acid, which can exist in combination both as a crystalloid and colloid, we have two series of compounds, silicates and cosilicates, the acid of the latter appearing to have an equivalent much greater (thirty-six times greater in one salt) than the acid of the former. The apparently small proportion of acid in a variety of metallic salts, such as certain red salts of iron, is accounted for by the high colloidal equivalent of their bases. The effect of such an insoluble colloid as Prussian blue in carrying down small proportions of the pre-

cipitating salts, may admit of a similar explanation. (P. 221).

"The hardness of the crystalloid, with its crystalline planes and angles, is replaced in the colloid by a degree of softness, with a more or less rounded outline. The water of crystallization is represented by the water of gelatination. The water in gelatinous hydrates is aptly described by M. Chevreul as retained by 'capillary affinity,' that is, by an attraction partaking both of the physical and chemical character." (P. 222).

Graham, at the conclusion of his important work, gives an explanation of osmosis, which in the main agrees with the views of Liebig, published some time previously.

The contents of another valuble work of Graham will for the most part be given in the author's own words.

" On the Properties of Silicic Acid and other Analogous Colloidal Substances "

By THOMAS GRAHAM, F.R.S., Master of the Mint

(Received June 16, 1864) [1]

PRELIMINARY NOTICE

"The prevalent notions respecting solubility have been derived chiefly from observations on crystalline salts, and are very imperfectly applicable to the class of colloidal substances. Hydrated silicic acid, for instance, when in the soluble condition, is, properly speaking, a liquid body, like alcohol, miscible with water in all proportions. We have no degrees of solubility to speak of with respect to silicic acid, like the degrees of solubility of a salt, unless it be with reference to silicic acid in the gelatinous con-

[1] Thomas Graham, Proceedings of the Royal Society, June 16, 1864. (Also Pogg, Ann., 1864, Vol. CXXIII, pp. 529–541.)

dition, which is usually looked upon as destitute of solubility. The jelly of silicic acid may be more or less rich in combined water, as it is first prepared, and it appears to be soluble in proportion to the extent of its hydration. A jelly containing 1 per cent of silicic acid, gives with cold water a solution containing about 1 of silicic acid in 5000 water; a jelly containing 5 per cent of silicic acid gives a solution containing about 1 part of acid in 10,000 water. A less hydrated jelly than the last mentioned is still less soluble; and finally, when the jelly is rendered anhydrous, it gives gummy-looking, white masses, which appear to be absolutely insoluble, like the light dusty silicic acid obtained by drying a jelly charged with salts, in the ordinary analysis of a silicate.

"The liquidity of silicic acid is only affected by a change, which is permanent (namely, coagulation or pectization), by which the acid is converted into the gelatinous or pectous form, and loses its miscibility with water. The liquidity is permanent in proportion to the degree of dilution of silicic acid, and appears to be favored by a low temperature. It is opposed, on the contrary, by concentration, and by elevation of temperature. A liquid silicic acid of 10 or 12 per cent pectizes spontaneously in a few hours at the ordinary temperature, and immediately when heated. A liquid of 5 per cent may be preserved for five or six days; a liquid of 2 per cent for two or three months; and a liquid of 1 per cent has not pectized after two years. Dilute solutions of 0.1 per cent or less are no doubt practically unalterable by time, and hence the possibility of soluble silicic acid existing in nature. I may add, however, that no solution, weak or strong, of silicic acid in water has shown any disposition to deposit *crystals*, but always appears on drying as a colloidal glassy hyalite. The formation of quartz cry-

stals at a low temperature, of so frequent occurrence in nature, remains still a mystery. I can only imagine that such crystals are formed at an inconceivably slow rate, and from solutions of silicic acid which are extremely dilute. Dilution no doubt weakens the colloidal character of substances, and may therefore allow their crystallizing tendency to gain ground and develop itself, particularly where the crystal once formed is completely insoluble, as with quartz.

"The pectization of liquid silicic acid is expedited by contact with solid matter in the form of powder. By contact with pounded graphite, which is chemically inactive, the pectization of a 5 per cent silicic acid is brought about in an hour or two, and that of a 2 per cent silicic acid in two days. A rise of temperature of 1°.1 C. was observed during the formation of the 5 per cent jelly.

"The ultimate pectization of silicic acid is preceded by a gradual thickening in the liquid itself. The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid-transpiration-tube may be employed as a colloidoscope. With a colloidal liquid alterable in viscosity, such as silicic acid, the increased resistance to passage through the colloidoscope is obvious from day to day. Just before gelatinizing, silicic acid flows like an oil.

"A dominating quality of colloids is the tendency of their particles to adhere, aggregate, and contract. This idio-attraction is obvious in the gradual thickening of the liquid, and when it advances leads to pectization. In the jelly itself, the specific contraction in question, or *synaeresis*, still proceeds, causing separation of water, with the division into a clot and serum; and ending in the production of a hard stony mass, of vitreous struc-

ture, which may be anhydrous, or nearly so, when the water is allowed to escape by evaporation. The intense synaeresis of isinglass dried in a glass dish over sulphuric acid *in vacuo* enables the contracting gelatin to tear up the surface of the glass. Glass itself is a colloid, and the adhesion of colloid to colloid appears to be more powerful than that of colloid to crystalloid. The gelatin, when dried in the manner described upon plates of calc-spar and mica, did not adhere to the crystalline surface, but detached itself on drying. Polished plates of glass must not be left in contact, as is well known, owing to the risk of permanent adhesion between their surfaces. The adhesion of broken masses of glacial phosphoric acid to each other is an old illustration of colloidal synaeresis.

"Bearing in mind that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter, but more greatly developed in some substances than in others, it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions." (Pp. 335, 336.)

Graham goes on to say that certain fluid substances which exercise no pectizing influence on colloids, can totally or partially displace the combined water of colloidal silicic acid, without causing the coagulation of the colloid. Hydrochloric, nitric, acetic, and tartaric acids, sugar syrup, glycerin, and alcohol are in this class. He then describes the production of such a solution of silicic acid in alcohol and the *alcogel.*

"The *alcogel,* or solid compound, is readily prepared by placing masses of gelatinous silicic acid, containing 8 or 10 per cent of the dry acid, in absolute alcohol, and changing the latter repeatedly till the water of the hydrogel is fully replaced by alcohol. The alcogel is generally

slightly opalescent, and is similar in aspect to the hydrogel, preserving very nearly its original bulk. The following is the composition of an alcogel carefully prepared from a hydrogel which contained 9.33 per cent of silicic acid:

Alcohol	88.13
Water	0.23
Silicic acid	11.64
	100.00

"Placed in water, the alcogel is gradually decomposed—alcohol diffusing out and water entering instead, so that a hydrogel is reproduced. (Pp. 337, 338.)

"The compound of sulphuric acid, *sulphagel,* is also interesting from the facility of its formation, and the complete manner in which the water of the original hydrogel is removed. A mass of hydrated silicic acid may be preserved unbroken if it is first placed in sulphuric acid diluted with two or three volumes of water, and then transferred gradually to stronger acids, till at last it is placed in concentrated oil of vitriol. The sulphagel sinks in the latter fluid, and may be distilled with an excess of it for hours without losing its transparency or gelatinous character. It is always somewhat less in bulk than the primary hydrogel, but not more, to the eye, than one fifth or one sixth part of the original volume. This sulphagel is transparent and colorless. When a sulphagel is heated strongly in an open vessel, the last portions of the monohydrated sulphuric acid in combination are found to require a higher temperature for their expulsion than the boiling-point of the acid. The whole silicic acid remains behind, forming a white, opaque, porous mass, like pumice. A sulphagel placed in water

is soon decomposed, and the original hydrogel reproduced. No permanent compound of sulphuric and silicic acids, of the nature of a salt, appears to be formed in any circumstances. A sulphagel placed in alcohol gives ultimately a pure alcogel. Similar jellies of silicic acid may readily be formed with the monohydrates of nitric, acetic, and formic acids, and are all perfectly transparent.

"The production of the compounds of silicic acid now described indicates the possession of a wider range of affinity[1] by a colloid than could well be anticipated. The organic colloids are no doubt invested with similar wide powers of combination, which may become of interest to the physiologist. The capacity of a mass of gelatinous silicic acid to assume alcohol, or even olein, in the place of water of combination, without disintegration or alteration of form, may perhaps afford a clue to the penetration of the albuminous matter of membrane by fatty and other insoluble bodies, which seems to occur in the digestion of food. Still more remarkable and suggestive are the *fluid* compounds of silicic acid. The fluid alcohol or olein compound favors the possibility of the existence of a compound of the colloid albumen with olein, soluble also and capable of circulating with the blood.

"The feebleness of the force which holds together two substances belonging to different physical classes, one being a colloid and the other a crystalloid, is a subject deserving notice. When such a compound is placed in a fluid the superior diffusive energy of the crystalloid may cause its separation from the colloid. Thus, of hydrated

[1] This is not an instance of chemical affinity and chemical combination in the now adopted meaning of the word. See further on in this Chapter (Zs).

silicic acid, the combined water (a crystalloid) leaves the acid (a colloid) to diffuse into alcohol; and if the alcohol be repeatedly changed, the entire water is thus removed, alcohol (another crystalloid) at the same time taking the place of water in combination[1] with the silicic acid. The liquid in excess (here the alcohol) gains entire possession of the silicic acid. The process is reversed if an alcogel be placed in a considerable volume of water. Then alcohol separates from combination, in consequence of the opportunity it possesses to diffuse into water; and water, which is now the liquid present in excess, recovers possession of the silicic acid. Such changes illustrate the predominating influence of mass.

"Even the compounds of silicic acid with alkalies yield to the decomposing force of diffusion. The compound of silicic acid with one or two per cent of soda is a colloidal solution, and, when placed in a dialyzer over water *in vacuo* to exclude carbonic acid, suffers gradual decomposition. The soda diffuses off slowly in the caustic state, and gives the usual brown oxid of silver when tested with the nitrate of that base.

"The pectization of liquid silicic acid and many other liquid colloids is effected by contact with minute quantities of salts in a way which is not understood. On the other hand, the gelatinous acid may again be liquefied, and have its energy restored by contact with a very moderate amount of alkali. The latter change is gradual, 1 part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry), in 60 minutes at 100° C. Gelatinous stannic acid also is easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again

[1] See note on p. 52.

from it by diffusion into water upon a dialyzer. The solution of these colloids, in such circumstances, may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid, but alkaline. Liquid silicic acid may be represented as the 'peptone' of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali may be spoken of as the peptization of the jelly. The pure jellies of alumina, peroxid of iron, and titanic acid, prepared by dialysis, are assimilated more closely to albumen, being peptized by minute quantities of hydrochloric acid.

"*Liquid Stannic and Metastannic Acids.* Liquid stannic acid is prepared by dialyzing the bichlorid of tin with an addition of alkali, or by dialyzing the stannate of soda with an addition of hydrochloric acid. In both cases a jelly is first formed on the dialyzer; but, as the salts diffuse away, the jelly is again peptized by the small proportion of free alkali remaining; the alkali itself may be removed by continued diffusion, a drop or two of the tincture of iodin facilitating the separation. The liquid stannic acid is converted on heating it into liquid metastannic acid. Both liquid acids are remarkable for the facility with which they are pectized by a minute addition of hydrochloric acid, as well as by salts.

"*Liquid Titanic Acid* is prepared by dissolving gelatinous titanic acid in a small quantity of hydrochloric acid, without heat, and placing the liquid upon a dialyzer for several days. The liquid must not contain more than one per cent of titanic acid, otherwise it spontaneously gelatinizes, but it appears more stable when dilute. Both titanic and the two stannic acids afford the same classes of compounds with alcohol, etc., as are obtained with silicic acid.

"*Liquid Tungstic Acid.* The obscurity which has so long hung over tungstic acid is removed by a dialytic examination. It is, in fact, a remarkable colloid, of which the pectous form alone has hitherto been known. Liquid tungstic acid is prepared by adding dilute hydrochloric acid carefully to a five per cent solution of tungstate of soda, in sufficient proportion to neutralize the alkali, and then placing the resulting liquid on a dialyzer. In about three days the acid is found pure, with the loss of about twenty per cent, the salts having diffused entirely away. It is remarkable that the *purified* acid is not pectized by acids or salts even at the boiling temperature. Evaporated to dryness, it forms vitreous scales, like gum or gelatin, which sometimes adhere so strongly to the surface of the evaporating dish as to detach portions of it. It may be heated to 200° C. without losing its solubility or passing into the pectous state, but at a temperature near redness it undergoes a molecular change, losing at the same time 2.42 per cent of water. When water is added to unchanged tungstic acid it becomes pasty and adhesive like gum; and it forms a liquid with about one fourth its weight of water, which is so dense as to float glass. The solution effervesces with carbonate of soda, and tungstic acid is evidently associated with silicic and molybdic acids. The taste of tungstic acid dissolved in water is not metallic or acid, but rather bitter and astringent. Solutions of tungstic acid containing 5, 20, 50, 66.5, and 79.8 per cent of dry acid possess the following densities at 19°: 1.0475, 1.2168, 1.8001, 2.396, and 3.243. Evaporated *in vacuo* liquid tungstic acid is colorless, but becomes green in air from the deoxidating action of organic matter. Liquid silicic acid is protected from pectizing when mixed with tungstic acid, a circumstance probably

connected with the formation of the double compounds.

"*Molybdic Acid* has hitherto been known (like tungstic acid) only in the insoluble form. Crystallized molybdate of soda dissolved in water is decomposed by the gradual addition of hydrochloric acid in excess without any immediate precipitation. The acid liquid thrown upon a dialyzer may gelatinize after a few hours, but again liquefies spontaneously, when the salts diffuse away. After a diffusion of three days, about 60 per cent of the molybdic acid remains behind in a pure condition. The solution of pure molybdic acid is yellow, astringent to the taste, acid to test-paper, and possesses much stability. The acid may be dried at 100°, and then heated to 200° without losing its solubility. Soluble molybdic acid has the same gummy aspect as soluble tungstic acid, and deliquesces slightly when exposed to damp air. Both acids lose their colloidality when digested with soda, for a short time, and give a variety of crystallizable salts." (P. 338–341.)

2. Colloidal Sulphids and Metals: Order of Their Discovery

If, in our present state of knowledge we consider the chief moot question as to the nature of colloidal solutions, it will at once be seen that the conflict of opinions had its origin in the irreversible colloids, and is in part due to a mutual misunderstanding. As stated in Chapter I, chemists designated as suspensions, only coarse, heterogeneous subdivisions, which settle of their own accord, but considered clear non-settling subdivisions as solutions; while some physicists called subdivisions of this latter class suspensions. Soon, however, fluids were found which were intermediate between the suspensions

and the solutions of the chemists. These formed the subject of differences of opinion, and at the same time were the starting-point of investigations which afforded a partial, but still very incomplete, insight into the nature of hydrosols.

Thus Berzelius regarded the hydrosol of arsenic sulphid as a suspension, because of its property of settling after standing a while.

Colloidal Sulphids. H. Schulze, whom we must thank for the first thorough investigation on colloidal sulphids (1882), concluded from his observations on colloidal arsenic sulphid that this fluid is by no means identical with ordinary levigated arsenic sulphid; but rather that its action and properties coincide in many important points with the hydrosols of ferric oxid, aluminium, etc., described by Graham, and therefore had no hesitation in calling them solutions. The marked cloudiness of his fluid, Schulze considered fluorescence; for he should have been able to see suspended particles of arsenic sulphid under the microscope, while his fluid by microscopic examination appeared perfectly homogeneous.[1] In order to explain the existence of solutions of the insoluble As_2S_3, Schulze (just as had Graham), assumed the existence of allotropic modifications.

Schulze's communication on the colloidal sulphids of arsenic and antimony were soon followed by further work on colloidal sulphids, especially that of Spring (1883), and later by that of Winssinger. Spring's article on colloidal copper sulphid led Ebell (1883)[2] to point

[1] Schulze cannot be blamed for not differentiating between diffuse dispersion and fluorescence, for the method of differentiating these two was practically unknown to the chemical fraternity.

[2] Berichte d. Deutschen chem. Gesell., 1883, Vol. XVI, pp. 1142–43; also Spring and de Boeck, Bull. de la Soc. chim., 1887 [2], Vol. XLVIII, p. 165.

out the analogy between colloidal sulphids and the finest levigated ultramarine, which no longer settles.[1] Ebell fortunately had at his disposal a fluid which may be considered as an intermediary between hydrosols and suspensions. This fluid contained particles which were still visible under the microscope, but which upon long standing settled only partially, or not at all. In layers about 2 cm. thick the fluid was transparent, and appeared clear to transmitted light. As is the case with many irreversible hydrosols, it left, when evaporated on the water bath, a shining varnish which could not be levigated in water to the original state of fineness; having in mind that its particles are microscopically visible, its relation to suspensions is indicated by the fact that precipitates produced by salts assume their original state of subdivision in pure water. (This fluid should be further examined ultramicroscopically for the presence of finer particles.) Remembering that this fluid is obtained by the levigation of the crude product in the second step in ultramarine manufacture, and that in the first step clay is for a long time roasted with alkali sulphate and carbon, it will not appear improbable that we have here a partially coagulated hydrosol, and that the particles visible under the microscope are already flocks, formed by the clotting together of incomparably much smaller particles under the influence of salts, which are at once brought into solution upon leaching the melt. Further evidence of this is its slow settling and the transparency of the fluid, a property common to levigated hydrogels.

Spring, who originally held with Schulze that colloidal sulphids were especial water soluble modifications, later agreed with the opinion of Ebell and other investigators, that in this case there was an extreme subdivision of the

[1] Berichte d. Deutschen chem. Gesell., 1883, Vol. XVI, pp. 2429–2432.

material; but in addition he made the most important observation,[1] based upon the work of Picton and Linder, and his own work on optically clear water, that many other colloidal solutions and also solutions of many crystalloids show the same lack of optical homogeneity as do the irreversible hydrosols, which were chiefly suspected of being heterogeneous.

Colloidal Silver. An excellent experimental investigation of the water-soluble modifications of silver was worked out by Carey Lea, and at that time it attracted general attention. In 1889 Lea succeeded in producing a water-soluble substance containing over 95 per cent of silver. It was natural to regard this water-soluble form as an allotropic modification of the metal. The name chosen by Lea assumed as much.

Prior to Lea, in 1887, O. Loew[2] and Muthmann[3] had prepared colloidal silver, and Muthmann had observed that the substances assumed by Wöhler and others to contain silver suboxid, were mixtures of silver oxids with metallic silver. He had furthermore dissolved out with ammonia the colloidal silver contained in such reduction products, established its constitution, and described its properties.

Muthmann also observed that certain other amorphous bodies, such as ferric hydroxid and molybdic dioxid hydrate had similar properties to the finely divided silver described by him, and he considered it not improbable that the various modifications of silver which he noticed betokened variations in molecular condition. The connection of this work with Graham's appears to

[1] W. Spring, Bull. de l'Acad. roy. de Belgique, 1899 (Cl. de. sc.), No. 4, pp. 300–315.

[2] Loew, Berichte, 1883, Vol. XVI, p. 2707.

[3] Muthmann, Berichte, 1887, Vol. XX, p. 983.

have escaped Muthmann, for he makes no reference to it in his paper, and besides, the only correct terminology for his fluids "colloidal solutions or hydrosols" is not used by Muthmann.

In the year 1890 Prange observed that the allotropic silver of Carey Lea could be regarded as a water-soluble colloidal form of this metal, and gave a series of proofs as to the colloidal nature of its solution. Since Prange's publication Lea's silver has been generally and properly called colloidal silver.

Conflicting Views Regarding the Nature of Irreversible Hydrosols. Barus and Schneider[1] in a most thorough paper, oppose the idea that colloidal silver is an allotropic modification of the metal. Without being quite able to disprove the presence of an allotropic modification, both investigators pointed out the analogy between the properties of the colloidal silver and those of suspended clay particles, and adduced much evidence to show that the silver is present in a fine state of subdivision. Barus and Schneider regard colloidal solutions as true suspensions, in which the sedimentation can be calculated from the mechanical laws of falling bodies based upon the radius of the particles, viscosity of the medium, difference in density between both substances, and the acceleration due to gravity.

They came to the following conclusion:

"Taking all facts into consideration, we think we may conclude that the view that colloidal silver consists of extremely finely divided little particles of normal silver which may be considered as continuing to float, because of the viscosity of the solvent, is in no way contrary to the observed properties of colloidal solutions. Inasmuch as there are hardly any good reasons for the assump-

[1] Zeitschr. f. physikal. Chemie, 1891, Vol. VIII, p. 297.

tion of an allotropic molecule, it is simpler to adhere to the normal molecule. The same applies to colloidal solutions in general." [1]

From a little known criticism of this work by two English scientists, Picton and Linder (1892), who, among other things, deserved credit for having shown that by continued subdivision of sulphids, colloidal solutions exhibiting osmotic pressure and diffusibility nearly approaching those of the lower colloids can be obtained from mechanical suspensions, we quote only one part [2] having reference to the work of Barus and Schneider:

"The evidence upon which most stress is laid in the above quoted paper (of Barus and Schneider) seems to us to be decidedly inconclusive. It is also noteworthy that throughout this paper there is an assumption that if the colloidal solutions contain very finely divided particles, the solution is a fact of mere mechanical suspension and nothing more. This is evident, too, from their method of calculating the size of the suspended particles. An assumption of this kind seems to us quite irreconcilable with fact."

Although Picton and Linder completely agree with Barus and Schneider that in colloidal solutions there is the most extreme subdivision of the substance, and in their beautiful experimental work give much evidence therefor, they by no means favor the explanation given by the latter. They oppose the conception that colloidal solutions are mere mechanical suspensions, and conceive the particles contained in hydrosols to be

[1] Wernicke has also expressed the same idea. Wied. Ann., 1894, N. F., Vol. LII, p. 515.

[2] Picton and Linder, Solutions and Pseudo-Solutions, J. of Chem. Society, 1892, p. 148.

large molecular aggregations. (Picton and Linder, p. 169.)

Picton and Linder produced four kinds of arsenic sulphid: As_2S_3 α, β, γ, δ, of which α is the largest particle (still visible microscopically) and δ is the smallest. As_2S_3 α, β and γ are retained upon filtration through a porcelain cell, while δ is not. In this case no adsorption takes place, for if As_2S_3 were adsorbed by porcelain, δ would also be retained by it; the particles of the first three hydrosols are much too large to pass through the filter.

While hydrosols α and β do not diffuse, hydrosols γ and δ exhibit distinct diffusibility. A four per cent solution of arsenic sulphid had an osmotic pressure equivalent to 17 mm. of water.

Picton and Linder are of the opinion that the particles which diffuse and produce osmotic pressure are identical with those which, upon Tyndall's test, betray their existence by polarization. This has an important bearing on the objections which can be urged (see this chapter further below) against the applicability of the osmotic method for the determination of molecular weight.

If diffusibility were due to the presence of crystalloids or else to a partial crystalloid solubility of the arsenic sulphid, then the same cause would also operate in the case of the coarser hydrosols, which, however, show no trace of diffusion and no osmotic pressure.

That in $As_2S_3\delta$ the whole mass of the arsenic sulpid consists of smaller particles than the others, is self-evident from the fact that it passes through a clay cell, while the other three hydrosols are held back.

It should be observed that Linder and Picton, even in their first communication, pointed out that all col-

loidal sulphids contain a certain quantity of sulphureted hydrogen which can be partially driven off by the addition of acid. Linder and Picton regard this sulphureted hydrogen as chemically combined, and consider the colloidal sulphids to be complex chemical compounds of sulphid with H_2S. Thus on the basis of their analyses they assign to cupric sulphid the formula $9CuS,HS$ or $22CuS,H_2S$; to zinc sulphid the formula $7ZnS,H_2O$ or $12ZnS,H_2S$; to mercuric sulphid $31HgS,H_2S$ and $62HgS,H_2S$. Further, colloidal arsenic sulphid, for which above the abbreviated formula As_2S_3 has been used, contains combined sulphureted hydrogen in the proportion of 8 (or 16) $As_2S_3:1H_2S$. The solubility of some sulphids in sulphureted hydrogen is attributed to the formation of complex hydrosulphids.

Jordis, as is well known, recently adopted a quite similar view concerning colloidal silicic acid (and colloids in general), in that he regards, for instance, the silicic acid hydrosol to be not a colloidal solution of silicic acid, but a solution of a chemical compound of the same.[1] Besides, even Graham regarded solutions of colloidal silicic acid in a little alkali as silicates, and called them colli-silicates or co-silicates.

New Hydrosols of the sulphid group have been made in large numbers by Winssinger (almost all of them colloidal sulphid solutions), by E. A. Schneider (colloidal gold sulphid and tin sulphid among others), colloidal oxids by Grimaux, Spring, Biltz, and others.

Hydrosols of Metals have been produced by Faraday, Lea, O. Loew, Muthmann, Lobry de Bruyn, Zsigmondy, Lottermoser (Hg, Bi, Cu, Pt, Pd, Rh), and by Bredig, by the very original method of atomizing metal by means

[1] Jordis, loc. cit., Chapter III above and Chapter XXI.

of an electric arc under water (Pt, Au, Pt, Ag, Cd, etc.). The numerous metallic hydrosols which Bredig has prepared in this manner were used by him in a very valuable chemico-contact investigation, the object of which was to throw new light on a series of hitherto unexplained phenomena which had been observed with organic ferments and enzymes. The analogy is so close that many of the same substances which are known as powerful blood poisons, and inhibit the catalytic action of the blood, also act as powerful "poisons" in hindering the catalytic action of colloidal platinum or gold.

An important method for the manufacture of high percentage and reversible hydrosols is that of Paal,[1] who succeeded in producing among other things a colloidal gold soluble in alkali and containing more than 93 per cent Au.

Recent investigators, Gutbier, Küspert, Henrich, Billitzer, Blake, Donau, and others, by extending known methods, have largely increased the number of methods for the production of metallic hydrosols, and among other things have shown that numerous reducing agents are suitable for this purpose, for example, any energetic reducing agent which does not of itself coagulate the hydrosol, or which exercises a protective action (Schutzwirkung), is adaptable for the production of hydrosols of the noble metals or analogues of the purple of Cassius, providing the essential well-known conditions are observed: sufficient dilution and extreme purity of the reagents, or the use of protective colloids which prevent the individual particles from coalescing.

Worthy of note is the method discovered by Donau for the production of colloidal gold by bubbling carbon

[1] Paal, Berichte, 1902, Vol. XXXV, p. 2236.

monoxid through a dilute solution of chlorid of gold, in which case no protective colloids can be formed.[1]

Purple of Cassius. A whole literature exists regarding the ammonia-soluble deep red precipitate known as the Purple of Cassius, which is obtained by mixing dilute solutions of chlorid of gold and stannous chlorid. As this substance has acquired significance because it gives an insight into many colloids, I must devote some space to it, even if I can mention only the most important points.[2]

Even in the time of Berzelius there existed two different ideas regarding the nature of this substance. Berzelius himself writes regarding it in his "Text Book of Chemistry":[3]

"It is not yet established what is the condition of the gold in the purple of Cassius. Some chemists consider it to be metallic and only mixed with the tin oxid. When, however, a gold salt which is mixed with any powder is reduced, the mixture gives a brick red powder which does not appear metallic and does not, furthermore, have the clear, transparent color of the purple; and if the purple is roasted in a small retort, it acquires the same brick-red color, indicating that the gold, upon roasting, has again assumed the metallic form."

And further (page 245):

"That the purple contains neither metallic gold nor

[1] The resemblance of this gold solution to those here described (Chapter VIII) is very great. The somewhat greater sensitiveness of Donau's gold soluton might be ascribed to its larger content of hydrogen ions. Donau, Wien. Akad. Ber., Vol. CXIV. Abt. IIa, 1905.

[2] A more detailed discussion will be found in my article: The Chemical Nature of the Purple of Cassius. Liebig's Ann., 1898, Vol. CCCI, pp. 362–387.

[3] Second Edition, translated by Blöde and Palmstedt, 1823, Vol. II, p. 244.

oxid is evident from the fact that it dissolves in ammonium hydrate, which would leave undissolved the admixed metal, or would form fulminate of gold with the oxid. The ammonia solution is a dark red fluid, from which the purple precipitates as a jelly upon spontaneous evaporation of the ammonia."

On the basis of his investigations, Berzelius regarded the purple as a chemical combination of tin sesquioxid (zinnoxyduloxid) with purplish oxid of gold. As may be seen, Berzelius laid great stress upon the homogeneity of the purple, and just because of the clear, transparent color of the precipitate and its solubility in ammonia, he was led to hold that the purple is not a mixture of finely divided gold and stannic acid, the color of which was known to him.

It is of the utmost importance to bear in mind that a greater part of inorganic chemistry was developed at a time when such ideas held sway, and a considerable number of substances which were called chemical compounds, would to-day be considered as colloidal mixtures or compounds, or as colloidal solutions, or as absorption compounds.

Later, many workers took up the moot question as to the nature of the purple of Cassius—I mention only Gay-Lussac, Debray, Golfier Besseyre, Müller—without reaching any final conclusion, for the chief point of Berzelius, the solubility of the purple in ammonia, was not cleared up. E. A. Schneider was the first correctly to explain the purple of Cassius as a mixture of the hydrosols of gold and stannic acid, and quite independently I was able to prove that the purple is not a chemical combination, by synthesizing it from its constituents.

By simple mixture of the hydrosols of gold and stannic acid I produced the purple of Cassius with all of its

usual properties. That the stannic acid in this case does not enter into a chemical reaction with the gold, is evident, firstly, from the indifference of metallic gold to colloidal stannic acid and similar bodies, and secondly, from the fact that by the presence of the stannic acid neither the absorption spectrum nor the intensity of the color of the colloidal gold changed in the least. These changes would have appeared if the gold had entered into chemical combination (as by treatment with chlorin, potassium cyanid, etc., whereby the red color vanishes in a short time). Nevertheless the presence of stannic acid has effected a profound change in the behavior of the gold toward reagents; it suffers no color change[1] upon the addition of electrolytes, but precipitates together with the stannic acid as a purple-red ammonia-soluble gelatinous precipitate, and in this respect acts as if it were chemically combined with the stannic acid.

Colloidal Mixtures which have Simulated Chemical Compounds. The extensive experiments which led to the result above set forth, were begun with the belief that they were to settle a principle of general application. When, therefore, it was possible to prove beyond doubt that the purple of Cassius is not to be considered a chemical compound, as the most brilliant chemist of his time had assumed, it at once became questionable whether a very large number of substances which had been called chemical compounds really were such. At the beginning of my investigations, I myself considered it probable that this was a case of a chemical compound

[1] As is well known, pure red gold hydrosols are immediately coagulated by the addition of electrolytes with the production of a blue color, and subsequently deposit metallic gold; the purple of Cassius acts quite differently (see pp. 13, 14, and 78).

of acid character, which owed its solubility in ammonia to the formation of a soluble salt; but I was led to the conclusion that it was an intimate mixture of colloidal gold and colloidal stannic acid, or a "colloid-compound" of gold and stannic acid, owing its solubility to the peptisizing action of the alkali. Making use of the language of the old chemists, I expressed the generalization of these facts in the following sentence: A mixture of colloidal substances can, under certain conditions, act like a chemical compound, and the properties [1] of the one substance in such a mixture can be masked by the other.[2]

I chose the expression "colloidal mixture" in order to lay particular stress on the fact that this is not a case of combination in a chemical sense. Later, in conjunction with van Bemmelen's expression "absorption compound," I used the expression colloid-compound [3] for

[1] By "properties" is here meant chiefly behavior with reagents.

[2] Bredig (Anorganische Fermente, 1st ed., p. 20) has taxed me with basing my definition upon a loose conception of chemical combination. In reply I might simply remark, that a long-established idea cannot be overturned by the mere dictum of a new definition. A chemist whom it was desired to convince, upon the basis of a definition, that a substance described as a chemical compound by the highest authorities, really was not one, would rather doubt the accuracy of the definition in question than assume that the authorities were in error, especially when the proof was not based upon experimental grounds. An old-established means of discrimination between a mixture and a chemical compound, and one used by Berzelius in this case, is that the constituents of the former can be easily separated by means of solvents, while those of the latter cannot. I recall only the well-known example of iron and sulphur: from the mixture of both substances the sulphur (or the iron) may be removed by a variety of solvents, which is not the case with the combination FeS. That in the case of colloids every characteristic cannot be applied to distinguish between mixtures and chemical compounds will be shown by the substance of my work, and is indirectly expressed by the above definition.

[3] Zsigmondy, Verh. d. Gesell. Deutscher Naturforcher u. Aerzte (Hamburg), 1902, pp. 168-172.

colloidal mixtures in which both constituents are colloids, in order to express the intimate union of both colloidal substances.

It must here be noted, however, that not only have colloid compounds or colloidal mixtures, in which two colloids are united, been erroneously described as chemical compounds, but so also have mixtures or absorption compounds of crystalloids with colloids, as well as colloidal solutions of various substances, especially of metals in fused salts.

Thus Kirchhoff and Bunsen,[1] and later H. Rose,[2] describe a blue potassium subchlorid K_2Cl, which, upon stirring in water, decomposes into KCl and KOH with the evolution of hydrogen. It is very probable that this is a case of a colloidal solution of potassium in potassium chlorid, all the more so as Bronn[3] has shown that in all probability the red and blue solutions of potassium, sodium, etc., in ammonia are most probably colloidal. The same applies to sodium subchlorid Na_2Cl, described by H. Rose, and to rubidium and caesium subchlorids (Kirchhoff and Bunsen). These subchlorids interfere with the electrolysis of fused salts, and the metals dissolve in the molten mass producing the color. It is worthy of notice that Bunsen and Kirchhoff (as well as H. Rose) were led by the homogeneous appearance of their molten salts, "which neither to the naked eye nor under the microscope show the slightest trace of metallic substance," to assume that they were chemical compounds.

Recently R. Lorenz[4] has pointed out the analogy

[1] Kirchoff and Bunsen, Pogg. Ann., 1861, Vol. CXIII, p. 345.
[2] H. Rose, Pogg. Ann., 1863, Vol. CXX, p. 1.
[3] Bronn, Drude's Ann., 1905, Vol. XVI, p. 166.
[4] R. Lorenz. A complete collection of the observations of R. Lorenz

between these "compounds" and the "metal fog" (which also interrupts the electrolysis of fused salts), and it can be considered as almost proved that in this case too there is a colloidal solution of the metal in the fused salt.

From the above it seems probable that with a number of substances which have been described as chemical individuals, the chemical compounds in question do not exist. In part, the proof of this has already been furnished by means of individual substances, by various investigators—each independent of the other.

As examples may be mentioned:[1]

(1) All substances in which one constituent is a metal, and the other a colloidal oxid, a colloidal salt or a protective colloid:

Purple of Cassius as a colloidal mixture of colloidal gold and colloidal stannic acid.

The purplish gold oxid and related compounds (Berzelius, Buchner), as colloidal gold with impurities.

The solution of aurous sulphite (observed by Krüss and Clemens Winkler), as colloidal gold reduced by SO_2 (Zsigmondy).

Silver-purple, as a mixture of colloidal silver and colloidal stannic acid, produced synthetically by Lottermoser.

Argentous oxid and its salts, described by Wöhler, v. d. Pfordten and others; explained by Muthmann as mixtures which owe their color to colloidal silver.

To this group of colloid compounds belong the many analogues of the purple of Cassius, which on account of

upon metal fogs, is found in his monograph, "Electrolysis of Molten Salts," Part II, published by W. Knapp, Halle a. S. (See p. 57 of his book.)

[1] The references to the literature are given partly in my article above cited, partly in Lottermoser "On Inorganic Colloids," Stuttgart.

their high metal content may be called colloidal metals. For example:

The colloidal silver of Carey Lea, the colloidal gold, silver, platinum, palladium, etc., of Paal; the colloidal mercury of Lottermoser and others.

(2) Many substances formed by the union of two colloidal oxids, and sometimes regarded as sesquioxids or as chemical compounds of an acid oxid with a basic one.

Thus Berzelius describes tin sesquioxid, and considers its solubility in ammonia as evidence of the existence of a chemical compound.[1] This substance can, however, be regarded as purple of Cassius in which the gold is replaced by stannic oxid.[2]

There are, besides, a whole series of stannic acids—intermediaries between ortho- and metastannic acids, each with its peculiar reaction, which may be regarded as colloidal mixtures or colloid compounds of the two extreme members of this group.[3] The number of apparent chemical compounds would be indefinitely increased if every such body were described as a special hydrate or as a special allotropic modification of stannic acid, and even to-day this is often done with other colloidal precipitates.

The characteristic behavior of tin towards nitric acid containing ferric nitrate, described by Lepéz and Storch, can be explained on the assumption of the presence of a colloidal mixture of ferric oxid and stannic acid in solution.

By mixing solutions of positive and negative hydrosols, as Picton and Linder, and Lottermoser, have shown, precipitates can be obtained which, when one of the

[1] Stannous oxid does not dissolve in ammonia.

[2] Zsigmondy, Liebig's Ann., 1898, Vol. CCCI, p. 386

[3] Zsigmondy, Ibid, p. 372.

constituents contains an acid, and the other a basic oxid, may easily be mistaken for a salt-like chemical combination of the two—which, indeed, has often been the case.

This point in particular has been elucidated by the research of W. Biltz,[1] who demonstrated the generality of these reactions. As Biltz very justly observes, the assumption of a salt-like compound is excluded if the negative constituent is metallic gold, which gives precipitates when mixed with positive colloids just the same as do other negatively conducted colloids.

The most important results of Biltz are the following: oppositely conducted hydrosols mutually precipitate each other without the addition of electrolytes; similarly conducted ones do not (with some exceptions in the case of negatively conducted colloidal solutions, of selenium and gold, for example, in which case Biltz assumes the existence of chemical reactions).

Biltz further found that in the mutual precipitation of oppositely conducted colloids, an optimum of the precipitative action is to be observed. If the favorable conditions of precipitation are exceeded on either side, no precipitation at all takes place. (Protective action.)

(3) Here belong the organic compounds of oxids with albuminoid substances and the like. Thus Paal[2] has shown that the alkaline solutions of the salts of heavy metals in protein substances contain the heavy metal, not, as has been assumed, in so-called organic combination, but as colloidal oxids, which are held in solution by the protective action of the albuminoid or its decomposition products.

All these determinations and facts serve to round out our knowledge of the absorption compounds, which is

[1] W. Biltz, Berichte, 1904, Vol. XXXVII, p. 1111.
[2] Paal, Berichte, 1902, Vol. XXXV, p. 2205.

based upon the extended and basic research of van Bemmelen,[1] the pertinent results of which we will try to express in two sentences:

Most of the hydrogels contain their water, not chemically combined, but absorbed (or "adsorbed"); hydrogels of ferric oxid, alumina, silicic acid, stannic acid, etc., are not hydroxids of these elements, but "absorption compounds" of oxid and water in varying proportions.

By absorption, hydrogels may take up and hold acids, alkalis, salts, etc., dissolved in water, in such quantity sometimes that the resulting products may be mistaken for chemical compounds.

Following the investigations of van Bemmelen, Biltz and Behre have recently shown[2] that the compound of arsenic acid with ferric oxid, which Bunsen considered basic ferric arsenite, $4Fe_2O_3$, As_2O_3, $5H_2O$, is as a matter of fact an absorption[3] compound in van Bemmelen's sense.

W. Biltz has added to this result some interesting observations on the action of toxins and antitoxins, and has shown that these reactions may be considered as absorption phenomena.

Further W. Pauli, developing the basic work of Ehrlich, makes evident the fact[4] that reaction between

[1] van Bemmelen, Landw. Vers. Stat., 1888, Vol. XXXV, pp. 69–136; Rec. Trav. Chim. Pays-Bas, 1888, Vol. VII, pp. 37–118; Zeit. f. anorgan. Chemie, 1894, Vol. V, p. 466; Ibid, 1896, Vol. XIII, p. 283; 1898, Vol. XVIII, pp. 14 and 98; 1899, Vol. XX, p. 185; 1900, Vol. XXIII, pp. 111 and 321; 1903, Vol. XXXVI, p. 380; 1904, Vol. XLII, p. 265.

[2] Berichte, 1904, Vol. XXXVII, p. 3138, communication from W. Biltz.

[3] Biltz and other investigators use for the most part the word "adsorption"; in order to honor van Bemmelen who has attained special prominence in this field, I use the customary term "absorption" chosen by him.

[4] Wolfgang Pauli, Wandlungen in der Pathologie durch die Fort-

toxin and antitoxin may be traced to the mutual influence of different kinds of colloids, and that this opens up a wide field for colloid chemistry.

According to the above research the number of apparent chemical compounds, in which colloids play a rôle, is very large. We may here distinguish between:

(1) Colloidal solutions of metals in crystalloids (for example, "sodium subchlorid," salts of "silver suboxid," "aurous sulphite," etc.);

(2) Absorption compounds, like the hydrogels themselves, or those in which a crystalloid is taken up by a colloid, which in particular have been carefully studied by van Bemmelen;

(3) Colloid compounds, in which two colloids combine to form a new mixture which cannot be separated by solvents without destroying the colloidal character.

Incidentally we might here remark that many, though by no means all of the phenomena of dyeing may be attributed to just such reactions of colloids with each other, or between colloids and crystalloids.[1] Color lakes are to be considered, some as colloid compounds, some as absorption compounds; only rarely is it the case that real chemical compounds or even solid solutions are formed.

Colloidal Gold. In the year 1857 Michael Faraday[2] described various colored liquids which he had produced by reducing gold chlorid solutions with phosphorus, liquids which to-day would be called colloidal solutions or hydrosols of gold, terms that Faraday could

schritte der allgemeinen Chemie. Jubilee Address. Vienna, 1905, M Perles.

[1] Compare for example Krafft, Berichte, 1899, Vol. XXXII, p. 1008; Zacharias, Zeitsch. f. phys. Chem., 1902, Vol. XXXIX, p. 468; Biltz, Gött. Nachr., 1904, No. 1.

[2] Faraday, Phil. Trans., 1857, p. 154.

not use since the idea "colloidal solution" did not yet exist.

His method was very crude, and yielded liquids appearing sometimes red, sometimes blue or violet, liquids which mostly deposited their gold content; but sometimes very stable hydrosols. Upon boiling, all these liquids underwent a marked change; they became darker, the red gave place to violet, the violet to blue; their cloudiness increased, and their permanence was correspondingly lessened; and a little while after boiling they all gave a deposit. To this deposit Faraday directed his particular attention; he proved in many cases that whether it was obtained from a boiled liquid or not, whether it showed a blue, violet, or red color, it was metallic gold, notwithstanding its lack of resemblance to the noble metal. These investigations led Faraday to the conclusion that the liquids owed their color to the extremely finely subdivided gold contained in them. He further showed by direct experiment (concentrating the sun's rays with a burning glass) the existence of a diffuse dispersion, which as often as not showed a gold color.

Faraday found excellent confirmation for the correctness of his conclusion in the fact, brought out independently of the above research, that pure metallic gold—which he produced as a thin coating on quartz and glass by the "electrical evaporation" of a gold wire in hydrogen, etc.—showed to transmitted light the same colors as the above described gold-containing liquids.

To that group of chemists for whom it would have had particular interest, Faraday's pregnant work has apparently remained entirely unknown—until 1898. I have read no paper on gold ruby glass or purple of Cas-

sius, in which Faraday was quoted.[1] For instance, a quotation may be given from the paper of E. A. Schneider[2] on the purple of Cassius:

"Of itself the hydrosol of gold is probably not permanent for more than a few minutes. Up to the present time all attempts to produce it direct, or from the purple solution, have been fruitless. Thus it was thought that by treating the purple solution with concentrated hydrochloric acid or concentrated sulphuric acid, and then dialyzing, that the stannic acid would be separated from the gold. As a matter of fact, this did take place, but the gold in the dialyzer was found to be in a coagulated condition, after the acid and resulting tin compound had diffused out. The presence of the tin hydrosol is therefore *absolutely necessary* for the existence of the gold hydrosol."

This was written by E. A. Schneider, who not only showed how to prepare colloidal silver in a particularly pure form, but also was very ingenious in producing other colloidal solutions. He discovered the hydrosols of several sulphids of the noble metals, organosols of silver, of gold sulphid, colloidal iron phosphate, etc.

From this it will be seen that it was by no means easy, as long as the essential conditions were unknown, to prepare the hydrosol of gold free from stannic acid, and as I did not know of Faraday's work, and was working with less energetic reducing agents than the phosphorus used by him, I was obliged to surmount all the difficulties which stood in the way of the production of a stable, sufficiently pure and homogeneous red colloidal gold solution.

[1] Just as little was he quoted by those investigators who investigated the nature of "silver suboxid" and similar substances.

[2] Zeitschr. f. anorg. Chem., 1894, Vol. V, p. 82.

A gold solution of such properties was absolutely necessary in order to finally settle the question of the chemical nature of the purple of Cassius.

It was only by a thorough search of the literature, which I undertook after the conclusion of my experimental work on this subject, but before its publication,[1] that I found Faraday's work, which I rescued from the oblivion into which it had fallen.

My colloidal gold solutions exhibited the necessary properties in the way of homogeneity and permanence, which chemists are wont to attribute to a solution in the usual acceptation of the term (see Introduction). The experiments which led to their production also taught me to know the influence exerted by certain impurities in the water on the properties of the gold hydrosol.

While certain colloids favor the formation of the red gold hydrosol remarkably, others, even if present only in traces, make it almost impossible to obtain a usable colloidal gold solution. To the former belong colloidal stannic acid, for example; because of its presence, the gold formed by reducing gold chlorid solution with stannous chlorid, yields, not a brown or black precipitate, but a red precipitate, the purple of Cassius. Another colloid which protects the *nascent* colloidal gold was discovered by Faraday, and called by him "jelly." Lobry de Bruyn[2] (1898), characterized gelatin jelly as a protective colloid (Schutzkolloid). Paal (1900) showed that lysalbinic acid and protalbinic acid possess the same protective properties.

For my purpose the absence of foreign colloids was necessary; it was only when I had secured a gold hydro-

[1] Liebig's Annalen, 1898, Vol. CCCI, p. 29.

[2] Rec. des Trav. Chim. d. Pays-Bas, 1900, Vol. XIX, p. 236.

sol free from detectable quantities of foreign colloids, that I could synthesize the purple of Cassius, and show how the reactions of colloidal gold solutions could be influenced by the presence of other colloids.

By the exclusion of protective colloids, however, the sensitiveness of the solution was increased to such an extent that I was obliged carefully to keep out the colloids present in most kinds of distilled water, which would destroy the hydrosol as soon as it was formed. (See also Chapter VIII.) This I did by repeated redistillation, using a silver condenser, or by freezing the distilled water several times.

The colloidal gold solution obtained by carefully following my directions, is bright red and very stable; in contradistinction to Faraday's fluids, it stands heating to the boiling-point without being thereby altered, and it remains practically unchanged for months, even years. Upon the addition of most electrolytes [1] it quickly changes to a blue color, and then deposits gold as an extremely fine powder. The presence of foreign colloids of certain kinds prevents the color change as well as the precipitation of gold. Very minute quantities sometimes answer, 0.0001 per cent of gelatin, for instance, which can by no means alter the viscosity of the fluid in any appreciable manner. Thus was disproved a correlated assumption which was thought to follow from certain observations of Faraday [2] or Lobry de Bruyn,

[1] Exceptions to this rule are ammonia, and potassium cyanid and ferrocyanid.

[2] Faraday had allowed gold chlorid to dry out with "jelly," and found that the jelly colored red by metallic gold showed no color change with salt in contradistincton to the "ruby fluids" made without jelly. Faraday, however, has not stated from what colloid the jelly was made. The fact also escaped him that the same action exerted by the stiff jelly can also be exerted by minute traces of a glue-like substance.

that the added colloid works by increasing the viscosity of the medium, and preventing the sedimentation of the gold; for it is not the sedimentation but the coagulation of the metallic gold that is prevented. In this case the gold and the protective colloid exercise on each other a reciprocal influence, to which I shall later recur.[1]

Protective Action of Many Colloids and the Gold Figure. By looking further into these reactions I was able to bring to light an almost unknown general property of many colloids, of preventing the coagulation of typical irreversible hydrosols; and further to establish a relative measure of this protective action on bright red colloidal gold solutions, by fixing the gold figure.[2]

It must here be mentioned, however, that A. Lottermoser and E. von Meyer had previously found that egg albumen and blood serum could completely or partially prevent the precipitation of colloidal silver by sodium chlorid;[3]

[1] Facts in this field of work have long been known (for example, the solubility in alkali of albuminates of the heavy metals; the property possessed by gelatin, of preventing the precipitation by hydrogen sulphid of sulphids of the heavy metals), but such protective action had for the most part either been designated as chemical reaction, or else it had been assumed that the viscosity of the colloid in question held in suspension the precipitate produced. That we are here dealing with a general property of colloids, for which a quantitative expression can be found, was, as far as my knowledge goes, first brought to light in the work referred to.

[2] Zeitsch. f. analyt. Chem., 1901, Vol. XL, p. 697. Not all colloidal gold solutions are suitable for this purpose. That obtained by reducing gold chlorid with phosphorus is not, for reasons to which I will later refer. It gives very different gold figures.

[3] Journal f. prak. Chem, 1897, N. F., Vol. LVI, p. 242. On this subject the authors say: "The cause of this fact we cannot yet state; the formation of silver albuminate seems to be excluded." In a reference to this paper in the Zeitsch. f. physik. Chem., 1898, Vol. XXVI, p. 368, signed with the initials W. O., it is stated as follows: "It is a medical fact that colloidal silver in salve form, etc., is taken up by the organism, although the salts present in the body-fluids

and that Lottermoser has followed up this reaction further.[1]

By the "gold figure" is meant the number of milligrams of colloid which are just insufficient to prevent the change to violet of 10 ccm. of bright red colloidal gold solution, by the addition of 1 cm. of a ten per cent solution of sodium chlorid.[2]

There is thus made evident an enormous difference between the individual colloids, as may be seen from the table on the next page.

In the paper referred to are given the conditions which must be followed in order to secure for any particular protective colloid, by the method mentioned, concordant gold figures. The influence exercised upon the gold figure by dilution, temperature, and length of the experiment, is stated. It is also shown that all solutions of protective colloids undergo change with the lapse of time, so that their effectiveness diminishes, in some cases so much that the protective effect vanishes.

Fr. N. Schulz and myself established the gold figures for several constituents of egg albumen obtained by fractional precipitation according to the practice of physiological chemists.[3] It appeared that the gold figure well serves the purpose of characterizing more exactly

precipitate the solutions of colloidal silver. The authors first state," etc., and W. O. in his remarks on this point says: "In this case there is probably a formation of complex silver compounds similar to the silver compounds with the imids; to such substances silver does not act like a noble metal, finally dissolving with ease under the influence of free oxygen."

[1] Journal f. prak. Chem., 1905, N. F., Vol. LXXI, p. 296.

[2] The protective action may be better expressed by the reciprocal of the gold figures. Thus carrageen would have a protective action of 1–2, gelatin 100–200, raw sugar 0.

[3] Hofmeister's Beiträge zur chem. Physiol. u. Pathol., Vol. III, pp 138–160 (1902).

TABLE I.—GOLD FIGURES OF SOME COMMERCIAL COLLOIDS

(According to ZSIGMONDY)

Colloid.	Gold Figures.	Remarks.
Gelatin	0.005–0.01	
Russian glue	0.005-0.01	
Cologne glue	0.005–0.01	
Bone glue	0.005–0.01	
Isinglass	0.01 -0.02	
Casein	0.01[1]	Aqueous solution made with a few drops of NH_3.
Egg albumen	0.15–0.25 0.1 -0.2	Two different commercial varieties.
Gum arabic, Ia	0.15–0.25	
" " , IIa	0.1	
" " , IIIa	0.5-4	
Irish moss	0.5–1	
Tragacanth	about 2	
Dextrin	6–12 10–20	Two commercial varieties.
Wheat starch	about 4–6[2]	
Potato starch	about 25[2]	
Sodium stearate	10	At about 60° C.
" "	0.01	At boiling point.
Sodium oleate	0.4–1	
Old stannic acid solution	∞	
Urea	∞ less than 500	At ordinary temperature. At boiling point.
Raw sugar	∞	
Gum arabic, selected in pieces	0.4–0.6	

the globulin, albumen, etc., and of testing for the presence of certain impurities. The great difference in the value of the gold figure of crystallized and amorphous albumen, will be seen from the table on the following page.[2]

Very marked was the action of a substance usually obtained in large quantity in the second albumin frac-

[1] Only once determined, without control.

[2] The addition of NaOH to albumins having low protective action increases it very considerably.

tion and called by us "impurity" This substance alone (without the presence of salts) colored the colloidal gold solution blue, and made it impossible to determine the gold figure of crystallized albumen, so long as the impurity was contained in it.

TABLE II.—GOLD FIGURES OF SEVERAL ALBUMIN FRACTIONS AND ALBUMOSES

Colloid.	Gold Figure.	Author.	Remarks.
Globulin	0.02–0.05	Schulz & Zsigmondy	Obtained from white of egg by fractional precipitation
Ovomucoid	0.04–0.08	"	
Crystallized albumen	2–8	"	
Amorphous albumen	0.03–0.06	"	
Fresh white of egg .	0.08–0.15	Schulz & Zsigmondy	
Albumin from Merck	0.1–0.3	"	
Heteralbumose	0.01–0.075	E. Zunz	Primary albumoses from Witte's peptone, isolated by Pick's method.
Protalbumose.....	1.60–3.36	"	
Synalbumose [1]	.....	"	
Witte's peptone [2]. . .			

By the excellent work of Zunz [3] have been determined the gold figures of the primary albumoses (product of the peptic digestion of albumen, which, in addition to secondary albumoses and peptones, occur in Witte's peptone for example). Zunz determined with great

[1] Synalbumose does not protect colloidal gold but colors it blue. According to Zunz, 0.64–2.24 mg. of synalbumose is enough to turn 10 ccm. of gold solution violet in the absence of salts. This reaction of synalbumose is prevented by the presence of protalbumose, casein, albumen, but not by heteralbumose despite its high protective action.

[2] Acts similarly to synalbumose, only it coagulates colloidal gold still more powerfully. 0.24–0.64 mg. of Witte's peptone have the same effect as 0.64–2.24 mg. of synalbumose. (Zunz.)

[3] Archives internat. de Physiologie, 1904, Vol. 1, p. 427.

accuracy the gold figures of protalbumose and heteralbumose, and made the very remarkable discovery that synalbumose alone changed colloidal gold solutions blue, just like the "impurity" before described.

Zunz has recently[1] tested a series of pure albumoses and peptones as to their behavior with colloidal gold solutions. He shows that, just like synalbumose, they almost all possess the property of turning the colloidal gold violet without the addition of electrolytes, but that the quantity necessary to do this varies from substance to substance.

The chief results are given in the following table:

Substance.	*Quantity of the Substance in mg which suffices to Change to Violet 10 cc. of the Colloidal Gold.*
Thioalbumose	2.60–4.00
Albumose, A II.	2.24–3.20
" B I	0.08–0.32
" B III. *a*	0.20–0.80
" B III. *b*	0.50–1.40
" B III. *c*	0.40–1.20
" B IV. *b*	0.80–1.60
" B IV. *c*	0.70–1.80
" B/C	0.80–2.80
" C I	1.60–3.20
Peptone, α	0.24–0.52
" βb	3.60–7.40
" βc	4.4 –8.20

Zunz has further found[2] that no relation exists between the action of albumoses and peptones upon colloidal gold, and the alteration by these substances of the surface tension of water.

According to Traube and Bodländer,[3] a 0.1 per cent solution of albumoses give 125.3 drops in the stalagmometer, while pure water gives 100, and a 2 per cent solution of egg albumen only 106.3 drops.

[1] E. Zunz, Bull. Soc. Roy. des sciences med. et nat., June 11, 1906.

[2] E. Zunz, ibid.

[3] Ueber die Unterscheidung von Eiweiss, Berichte d. D. Chem. Ges., 1886, Vol. XIX, p. 1871–6.

Whereas, therefore, albumen but slightly influences the surface tension, albumoses influence it very strongly, but to about the same extent among themselves; on the other hand their behavior with gold solution varies greatly, as can be seen from the table.

TABLE III

Substance.	*Gold Figure.*	*Number of Drops in the Stalagmometer as Compared with* 100 *Drops of Distilled Water.*
Heteroalbumose...	0.01 to 1.075	114.4
Protalbumose.....	0.6 to 3.36	113.6
Synalbumose.....	Produces a change in color (0.64–2.24 mg.)	113.7

In the additional paper [1] Zunz shows that there is no relation whatever between the behavior of turbid mastic solution with albumoses, and that of colloidal gold with the latter. Thus heteroalbumose and synalbumose precipitate turbid mastic solution, whereas the other albumoses do not possess this property. As may be seen from what precedes, heteroalbumose does not exercise a precipitative action on colloidal gold, but rather a protective action.

From these facts it is evident that the electric charges alone do not determine the reactions in question, for mastic and gold particles are both negatively charged. If the electric charges alone exercised the main influence, gold and mastic should react the same with the albumoses. But this is not the case, and we are therefore confronted with specific actions, whose nature is not yet completely understood.[2]

W. Biltz [3] determined the gold figures of several inorganic colloids, and Biltz, Much, and Siebert, those of several sera and antitoxins.[4] The authors use the gold

E. Zunz, Arch. internat. de Physiol., 1907, Vol. V., p. 245.

[2] Neither is there any connection with the diffuse dispersion of light. According to Zunz all proteoses (albumoses) exhibit an intense light-cone, whereas the peptones show only a faint bluish cone, which vanishes upon the insertion of a yellow disk.

[3] Berichte, 1902, Vol. XXXV, p. 4437.

[4] Experimentelle Beiträge zu einer Absorptions-theorie der Toxin-

figure in order to determine approximately the loss of albumen content upon shaking with iron oxid. It appeared that albumen solutions containing salt gave up less albumen to the iron oxid gel than did dialyzed ones. The physiological salt content, therefore, protects albumen to a certain extent against absorption by hydrogels.

The authors further found that the gold figures of nutritive bouillon and toxin solutions could not be closely determined, because even without the addition of electrolytes, they immediately produce a blue color in colloidal gold solutions, a reaction which corresponds with that of synalbumose and that of Witte's peptone (see above). It was pointed out by Biltz, Much, and Siebert, that this reaction appears to be characteristic for peptones.[1] The growth of bacteria changes the nutritive bouillon, so that it regains the property of a protective colloid.

As previously mentioned above, W. Biltz observed that oppositely charged colloids mutually precipitate each other when they are mixed in certain proportions; if an excess of one or the other colloid is used, then this excess acts as a protective colloid. Similar facts have been determined by Bechhold,[2] Neisser, and Friedmann,[3] in connection with the precipitation of mastic by positive hydrosols, dye solutions, and the like. Protective action also appears in the mutual precipitation of acid and basic dye-stuffs, if there is used an excess of either dye-stuff over and above the quantity necessary for precipitation.

neutralisierung. Behring's Beiträge zur experimentellen Therapie, 1904, No. 10.

[1] "Peptone" here refers to the commercial mixtures, not the peptones of the physiological chemist.

[2] Bechhold, Zeitschr. f. physik. Chem., 1904, Vol. XLVIII, p. 385.

[3] Neisser and Friedemann, Müchener med. Wochenschr., 1903, No. 11.

These facts lend interest to some observations I made several years ago, but which I have not been able as yet to study more closely. I found that colloidal gold and basic dyes like fuchsin (or methyl violet, methylene blue, etc.), sometimes precipitate each other quantitatively, but that the reaction between the two substances often failed to occur or else took place very incompletely. I then attributed this to the protective action of impurities, but it is very possible that in the unsuccessful experiments, I exceeded the optimum of precipitative action more accurately described by Biltz and other investigators. From the precipitate the dye can be extracted by alcohol (not, however, by water). There remained on the filter a gold colored powder which was not further investigated.

Other investigators have shown that the protective action of some few colloids extends to a certain degree even to coarser subdivisions.[1] Arthur Müller showed this in the case of a suspension of red phosphorus.[2] That this is only superficially analogous to the protection in the case of gold, is at once evident when the two kinds of protective action are compared. While 0.025–0.05 mg. of gelatin completely protect 50 ccm. of colloidal gold, on the other hand, 25 mg. of the same colloid (that is 500 to 1000 times as much) are insufficient to completely prevent the flocculation of 50 ccm. of phosphorus suspension by sodium chlorid. Furthermore, raw sugar prevents the precipitation of phosphorus, but not the color change of colloidal gold.

Recently Arthur Müller and Paul Artmann[3] deter-

[1] For instance Neisser, Friedemann, and Bechhold have determined protective actions in the case of suspensions of bacteria.

[2] Berichte, 1904, Vol. XXXVII, p. 11.

[3] Oestrr. Chemiker-Ztg., 1904, Vol. VII, pp. 149–151.

mined the smallest quantity of protective colloid necessary to prevent the precipitation of several irreversible hydrosols, As_2S_3, CdS, etc. I reproduce their table.

TABLE IV

Metal Sulphid Solution.			Smallest Quantity of Colloid in mg.					
Substance.	Strength in Per Ct.	Quantity used cc.	Casein	Gum, Arabic.	Glue.	Isinglass.	Albumen.	Dextrin.
As_2S_3	0.05	5	0.16	0.32	0.40	0.55	2.50	50
CdS	0.10	3	0.65	1.15	1.80	1.50	8.00	∞
Ag_2S	0.05	5	0.06	0.13	0.18	0.18	0.60	∞

From the table it will be seen that the protective colloids, gum, glue, dextrin, etc., exercise upon the colloidal sulphids a protective action similar to that exercised upon colloidal gold, but that the quantitative expression of the protective action varies with the colloid. As with gold, raw sugar exercises no protective action on sulphids. Müller and Artmann further observed that under certain conditions glue solutions yield precipitates with colloidal solutions of cadmium and arsenic sulphids.

Just as did Ebell in the case of the colloidal sulphids, and Barus and Schneider with colloidal silver, so Stöckl and Vanino [1] have tried to prove that colloidal gold is an instance of very fine suspension. As Bredig and Coehn [2] have already pointed out, and as may be seen from the above remarks, they have advanced no distinctly new idea. I myself had considered my fluids as profound subdivisions of the metal, as may be seen from

[1] Zeitschr. f. physik. Chem., 1899, Vol. XXX, p. 98.
[2] Zeitschr. f. physik. Chem., 1900, Vol. XXXII, pp. 129–132.

my first paper on this subject.[1] I must, however, object to the term suspension, for my fluids, because of their permanence and homogeneity, should be classed as colloidal solutions, and not as "suspensions," as at present understood by chemists.

The discussion between Stöckl and Vanino and myself led Lobry de Bruyn to make some very noteworthy remarks [2] regarding colloidal solutions. From the molecular weight of soluble starch, Lobry de Bruyn calculated the molecular diameter (approximately 5 $\mu\mu$) and called attention to the fact that, according to Lord Rayleigh, particles of this size are large enough to polarize incident light.

In concluding this section reference must be made to the valuable work of Schulze, Lottermoser and von Meyer, Picton and Linder, Coehn, Hardy, Spring, Billitzer, Quincke, Freundlich, and others, whose object was to determine the laws governing coagulation by electrolytes, and who by preference chose colloidal sulphids and metals as subjects of investigation. Taken in connection with the earlier work of Scheerer, F. Schulze Schloesing, Barus, and Bodländer, on the clearing of clay turbidity, these researches lead to a sharp distinction between flocculation and sedimentation,[3] and estab-

[1] Zeitschr. f. Elektrochem., 1898, Vol. IV, p. 546: "Dr. Bredig exhibited to us yesterday a series of interesting properties of the electric arc. For example, by atomizing metals under water he obtained dark-colored fluids in which the metal was so finely subdivided that it could be regarded as dissolved; but they are not solutions, because on long standing they lose part of their metal content. *If the metal is still further subdivided fluids are obtained which no longer settle, that is, collodial metallic solutions.* Up to the present Carey Lea's silver solution was the only one of this class known."

[2] Rec. des trav. chim. Pays-Bas., 1900, Vol. XIX, pp. 251–258.

[3] See for example, Spring, Bull. d. l'Acad. roy. de Belgique, 1900, No. 7, p. 468; see also note on p. 31.

lished the dividing line between the flocculation of clay turbidity and the coagulation of irreversible hydrosols (see Chapter I). That the two processes last referred to are not identical, has been shown in Chapter I. There is at present no unanimity of opinion as to the fundamental causes of coagulation, other than what follows from comparing the views of Billitzer, Quincke, Freundlich, and Jordis.

In passing, it may be remarked that electrolytes not only cause pectization or coagulation, but also peptization of colloids, and that a complete theory of colloids cannot consider only one of these processes. In these very processes, moreover, the nature of the subdivided substance and the presence of traces of foreign constituents (which may even arise from chemical action) influence to the greatest degree the behavior of the hydrosols, and as long as these conditions remain unexplained, generalizations can easily lead to error.

3. Some Questions Concerning the Nature of Hydrosols

The conviction has gradually gained more and more ground that colloidal solutions are in reality fine subdivisions of an originally solid substance, and there is a diversity of opinion as to whether the individual particles which polarize light are to be regarded as very large molecules in the sense of Picton and Linder and Lobry de Bruyn,[1] or as minute particles of an originally solid substance.[2]

[1] Compare also Nernst, Theoretische Chem., 3d. ed., p. 383.

[2] Another question as to whether the particles in hydrosols are solid or fluid, cannot at present be satisfactorily settled. Quincke assumes the latter condition. Compare Chapter XXI, wherein is briefly discussed the question propounded by Jordis, whether the same substance is present in hydrosols as in hydrogels.

In the first instance, the hydrosols in question would be considered as crystalloid solutions with very great molecular weight. In the latter classification, which is adopted by Bredig and others, they rank as heterogeneous according to the phase rule, but then it must be borne in mind that even the homogeneous solutions of the crystalloids are, as a matter of fact, only apparently homogeneous (see Introduction, p. 7).

Without doubt the question above referred to is theoretically of high interest; but at present great difficulties stand in the way of its satisfactory solution. As Bredig has brought out,[1] in the case of colloidal solutions the osmotic pressure (trennungsarbeit) can be referred to a partial crystalloid solubility of the colloid, to crystalloid impurities, to electric charge of the individual particles. So long as these influences are not individually determined, the molecular weight of the dissolved colloid cannot be safely deduced from the results of the osmotic method.

To decide the question whether some or all colloidal solutions possess large molecules, would be of particular importance for the kinetic theory; for it is just the very large molecules, the presence of which some investigators assume in hydrosols, which would most facilitate a purely experimental confirmation of important corallaries of that excellent theory.

From the results of numerous physio-chemical investigations, and quite independent of any theory, it is evident that the osmotic volume-energy [2] which, with crystalloids, dominates part of the phenomena, becomes of

[1] Anorganische Fermente, p. 11.

[2] Regarding the expressons volume-energy, surface-energy, distance-energy, see Ostwald, Grundriss der allgemeinen Chem., 3d ed., pp. 53, 247, 251.

less importance as compared to the influence of the electrical and chemical energy, or of "surface energy" ("Oberflächenenergie") [1] and perhaps of still other kinds of energy, as yet unknown. As the volume-energy[2] diminishes or disappears, the hydrosols correspond to real suspensions, but there is nevertheless an evident difference between the two types of subdivision last referred to. While with the former the electrical energy and the surface energy (Oberflächenenergie) form an important part of the total energy, and render possible reactions which are deceptively similar to chemical reactions, with the latter their influence yields to that of gravity. (See Chapter I). The action of coarse, suspended powders is determined rather by purely mechanical influences and the speed with which their particles sink to the bottom, can be calculated according to the laws of falling bodies.[3]

Before a comprehensive theory of colloidal solution can be promulgated, it will be necessary to determine in each special case by thorough experimental investigation, the influence of these forms of energy which are most important in the case of hydrosols; a good beginning has already been made in this direction. I need only recall here the work of van Bemmelen, Spring, Paterno, Barus and Schneider, Picton and Linder,

[1] This expression is set in quotation marks simply because it might easily lead to the assumpton that only the surface of the particles contained in hydrosols comes into play. In this case *the particles themselves* act upon each other and the surrounding medium, and the existence of this action can be demonstrated by numerous observations. Macroscopically considered, this same kind of energy comes into evidence as surface-energy.

[2] Which may be considered in the sense of Ostwald, Bredig, as well as in the sense of Lobry de Bruyn.

[3] See Barus and Schneider, loc. cit., p. 287.

Lobry de Bruyn, Coehn, Bredig, Bruni and Pappadà, Lottermoser, Biltz, Billitzer, Quincke, Friedemann, and others, which has much advanced our knowledge of colloids and also suggested questions that deserve attention.

If we regard hydrosols as extremely fine subdivisions of substances originally solid, certain other questions immediately arise, some of which can be solved by the aid of ultramicroscopy.

First. Are the particles contained in colloidal solutions independent of each other, or does the colloidal solution contain a network or honeycomb of threads or thin walls connected together? One would be led to the latter opinion by the assumption that the process of solution of a colloid is simply a matter of swelling up. We will see that this assumption is untenable, for as far as particles in hydrosols can be seen, they are freely movable.

Second. Do the particles float quietly in the fluid, or fall to the bottom under the influence of gravity; or have they a more or less rapid motion of their own? In the latter case, what is the nature of the motion, oscillatory or translatory? What are the dimensions of the paths described relative to the size of the particles? Is the motion a temporary one brought about in the removal of differences of concentration, or is it a continuous one?

Third. What color are the individual particles; can a relation be found between their size and color?

Fourth. What is the size of the individual particles? Is it possible by careful preparation to produce colloidal solutions so homogeneous that the bulk of the subdivided substance cannot be recognized by the best optical methods, or can their heterogeneity in all cases be made evident by means of a beam of light?

Questions of this kind will, in certain definite cases, be answered in the experimental sections which follow, in which will also be given the answer to a question which led to this investigation:

Faraday, as we know, observed in all gold hydrosols and ruby glasses which he investigated, the appearance of a diffuse dispersion. To him this was evidence that the gold in these fluids is not dissolved, but is present in fine subdivision. Evidence accumulated quite independently of Faraday, that the red colored substance in my fluids is metallic gold, led me to the same opinion reached by Faraday, namely, that we were dealing here with finely divided gold; nevertheless, upon the basis of my experience, I believed optical inhomogeneity to be an incidental characteristic of hydrosols, brought about by coarser particles in the otherwise homogeneously subdivided (that is, dissolved)[1] substances. Faraday's view was afterwards espoused by various investigators, especially by Bredig,[2] and extended to colloidal solutions in general. This very opposition led me to a searching investigation of the point in question. By means of ultramicroscopy I was able to decide the question in favor of the view held by Faraday, Bredig, and others. It was apparent that the gold particles which occasion the red color of the colloidal solution, are the same ones that polarize light.

On the other hand, it also became evident that the particles in the particularly clear colloidal gold solu-

[1] "Dissolved" in the sense of the definition of the word solution. Formerly, in conformity with the quite generally accepted view, I regarded solutions as subdivisions completely homogeneous, optically speaking. The investigations of Spring and Lobry de Bruyn on this subject (see Introduction) were then unknown.

[2] Bredig, Zeitschr. f. angew. Chem., 1898, No. 41.

tions closely approach molecular dimensions, and the optical inhomogeneity of these same solutions is hardly greater than that of many crystalloid solutions,[1] in both cases it is hardly observable.

[1] See Lobry de Bruyn, loc. cit.

CHAPTER IV

FACTS POINTING TO THE HOMOGENEITY OF GOLD HYDROSOLS. DEVELOPMENT OF ULTRAMICROSCOPY

As the opinion just stated was based upon a long series of experiments which I never published in detail, and do not now need to publish, since the question has been settled in another manner, I may here briefly repeat the grounds upon which this opinion rests.[1]

I do this for the particular purpose of showing the insufficiency of grounds of a similar nature, which may doubtless be urged in favor of the view that solutions in general are homogeneous.

"To begin with, my view was supported by the observation that although the majority of the hydrosols of gold (colloidal gold solutions), produced by me, for the most part showed a noticeable faint and diffuse scattering of incident light, they were sometimes very clear[2] and sometimes very turbid.

"Despite their varying appearance, all these fluids contained equal quantities of metallic gold, as I convinced myself by repeated analyses; they were red colored, and also showed approximately the same behavior toward reagents.[3]

[1] Zsigmondy, Verhandl. d. Deutschen physik. Gesell., 1903, Vol. V, p. 209.

[2] So clear that the light-cone is scarcely more perceptible than in distilled water.

[3] They were precipitated by electrolytes, with the development of a blue color. Upon quantitative test, however, they developed certain differences in their behavior with reagents, but not in their gold content.

"Since, then, these fluids showed in general the same mutual properties, and could in practice be differentiated from each other only by their greater or lesser turbidity, I assumed that the turbidity is not an essential, but an incidental characteristic of colloidal gold solutions, occasioned by the presence of larger particles.

"The turbidity always showed a more or less intense polarization, an evidence of the minuteness of the haze-producing particles even in very turbid fluids.

"The above view received further support from a quantitative test of the sensitiveness of the recognition of subdivided gold by means of the convergent beam of light, which showed that in very cloudy fluids (upon considerable dilution) even less than 10^{-8} mg. of gold could in this manner be recognized with the naked eye by the visible path of the convergent beam,[1] that is, a less quantity of substance than Kirchhoff and Bunsen could detect by means of spectrum analysis. My cloudy fluids containing 0.0005 per cent of gold were diluted 100 to 1000 fold; the colorless dilute fluids still continued to show a more intense light-cone than the undiluted, unclouded solutions containing 0.005 per cent.

"The addition of a minute quantity of the very turbid fluid to the perfectly clear one sufficed to endow the latter with the polarized dispersion of the former, as evidenced by means of the light-cone; and this made evident of how small a quantity of coarse gold particles is necessary to produce, in a gold solution assumed to be homogeneous, the diffuse dispersion referred to.

[1] Since in using sun or arc light the diffuse light-cone shown by distilled water exercises a detrimental effect, these tests were made with Welsbach light which produced no light-cone in the water I used for dilution.

"It must be acknowledged, however, that although the facts above referred to were favorable to my view, they gave no evidence of the existence of an optically clear gold solution. I hoped to be able to find out the truth by microscopical examination of the cone of light."

Before I carry this discussion further it might be here stated that microscopical investigation led to the solution of the question. This investigation showed that all the red-colored gold particles take part in the formation of the polarized cone of light,[1] and the greater or lesser cloudiness of the colloidal gold solution is due to the fact that the gold particles which produce the red color are larger in some cases and smaller in others.

This result, which contradicts the view earlier advanced by me, is of great significance in judging colloidal solutions in general.

By the observations of Fizeau[2] and of Ambronn[3] it was shown that very narrow light slits can still be seen even if their breadth is considerably less than the limit of microscopic resolvability. The narrower the slit of light the less the brightness of its microscopic image, whose breadth, however, from a certain point downward, no longer varies.

It seemed to me probable that the larger particles assumed to be present in gold hydrosols, whose previously mentioned property of dispersing transmitted light was known to me by the above experiments, could be made individually perceptible by a microscopic examina-

[1] But in the case of the almost homogeneous gold solutions, this conclusion cannot with certainty be reached; however, in this case too, the faint trace of a light-cone can be attributed to the gold present.

[2] Pogg. Ann., 1862, Vol. CXVI, p. 478.

[3] Wied. Ann., 1893, Vol. XLVIII, pp. 217-222.

tion of the light-cone; for if the small particles reflected enough sunlight, even if their size was below the limit of microscopic resolvability, they would, just as were the narrow rays of light, be individually perceptible under the microscope and act to a certain extent as fragments of such light slits.

The microscopical investigation should also allow me to determine if the space between the coarser individual particles was optically clear or was filled with smaller gold particles.

As a matter of fact, in two very turbid fluids (AuP_8 and Au_{54})[1], by the use of sunlight and a magnification of about one hundred diameters, I could recognize the presence of thousands of shining gold particles, whose size, as was shown by a rough calculation based upon the distance of the particles from each other and the amount of gold present, must have been less than the wave-length of light. With ordinary illumination,[2] even with the best objectives, they were not perceptible.

The arrangement of the apparatus assembled for this purpose was the following:

The sun beams fell upon a mirror *S* (Fig. 1), were reflected from this into the lens *L*, which brought them to the focus at *b*, over which was arranged a low power microscope (Objective *A*, Huygens eyepiece 2 and 4).[3]

As early as April, 1900, solutions of glue, gelatin, tragacanth, stannic acid, and also a silver hydrosol of

[1] AuP_8 contained gold-glinting particles which settled in about eight days. Au_{54} was over half a year old and in this time had deposited but little gold. The particles were green in color, the fluid bright purple-red.

[2] And even by use of the dark field illumination then in use.

[3] Quincke had used side illumination with lamp or sun-light to observe the electric migration of starch grains, etc., under a magnification of 30 diameters. (Pogg. Ann., 1861, Vol. CXIII, p. 568.)

coarser subdivision, were examined by this method. In all these fluids, besides a general illumination of light-cone, individual particles could also be perceived;[1] but with the silver hydrosol there was visible a brilliant light-cone, which could be resolved into individual particles only upon extreme dilution. Of colloidal gold solutions, Au_{60} and AuP_3 were also investigated.

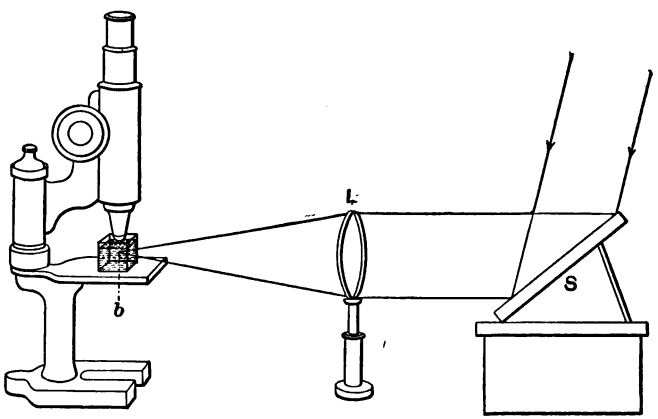


FIG. 1.

The slightly turbid gold solution Au_{60} (0.005 per cent Au) showed a green light-cone which vanished upon dilution without having revealed the presence of individual particles; the perfectly clear solution AuP_3 (0.005 per cent Au) only showed the presence of isolated gilded dust particles, while the space between them appeared optically clear. That this space still contained gold in an invisible form, was made evident by an experiment: upon addition of ordinary table salt the colloidal gold was coagulated, and then the fluid was thickly filled with brightly shining particles.

[1] Some of these individual particles polarize light, others on the contrary do not.

By these experiments were settled several questions of importance. Thus it was shown

1. That gold of various degrees of subdivision can be present in one fluid without settling;

2. That gold can be subdivided to the point of optical homogeneity.[1]

It was further shown experimentally that by the microscopic examination of a solar image formed in a fluid, particles can be discerned which are beyond the range of ordinary microscopy. I was convinced that by the use of better objectives the individual particles could also be seen in Au_{60} and similar fluids, and I determined to attempt, with the assistance of a specialist, to render such particles visible also. An investigation of this sort seemed all the more promising, as the preliminary experiments had shown that the color, brightness, and polarization of the individual particles show a great variation, which might serve more sharply to characterize them; furthermore, the colloidal gold solutions represented test objects which made it possible to ascertain approximately the average mass of the individual particles, from the mean distance between them, and the known gold content.

The perfected arrangement, bringing into use objectives of wider aperture, was later discovered by H. Siedentopf incidentally to our mutual work, on the basis of the principles developed by him for making visible ultramicroscopic particles. But first another problem had to

[1] Subsequent ultramicroscopic examination of gold ruby-glasses has shown, even in such homogeneous appearing subdivisions, the polarized light-cone can be seen by focusing objectives of higher aperture on the very outside layer of the preparation, and thus preventing, as far as possible, the absorption of the transmitted and reflected light. This precaution must be observed in the examination of apparently homogeneous colored solutions.

be solved. Because of the motion of their particles, colloidal gold solutions were not suitable for an *extremely exact* determination of the mass of the individual particles. For this purpose it was necessary to prepare a graduated series of subdivisions of gold containing fixed,[1] and, so far as possible, changeless particles. Test objects for this purpose I had made for me in the glass factory of J. L. Schrieber, at Zombkowice, Russia, incidentally to my attempt to work out a method for the manufacture of gold ruby glass which can be molded. After this preparation could be begun in collaboration with H. Siedentopf, an attempt to render visible finer ultramicroscopic particles, in which the work was so divided that H. Siedentopf carried out the construction and improvement of the apparatus for illumination, while I took charge of testing the apparatus constructed with my preparations, and of developing the method for the determination of size. The introduction of the bilateral slit, and the application of microscopic objectives for illumination by H. Siedentopf, were essential to rendering visible the smaller particles. Siedentopf also contributed the theory of making ultramicroscopic particles visible, and calculated the probable limits of their visibility.

It must be here noted that the limits of microscopic resolvability (limit of visible "separation") determined by Abbe and Helmholtz, is often confounded with the limit of "visibility." That isolated particles, whose diameter is a fraction of a wave-length of light, can still be seen, is expressly stated by Abbe himself. He writes in this connection:[2] "Such objects can be seen, no mat-

[1] For the purpose of making an exact count when determining the size of the gold particles.

[2] E. Abbe, Gesammelte Abhandlungen, Vol. I, p. 362. Jena, 1904, G. Fischer.

ter how small they may be; it is only a question of the contrast of the light effect, good definition of the objective, and sensitiveness of the retina." As may be seen, the results of our investigation are not at all, as has been often thought, in conflict with the statements of Abbe.

We received splendid assistance in our work from the numerous means placed at our disposal by the firm of Zeiss.[1] We were thereby enabled to work with the best objectives, and complete the mechanical development of the apparatus in a short time. Notwithstanding this, a year and a half of study was necessary to bring the apparatus to its present state of perfection.

[1] F. Auerbach states in his monograph: Das Zeisswerk und die Carl Zeiss-Stiftung in Jena 2d ed., Jena 1904. G. Fischer:

"Recently in the workshop of Carl Zeiss, their scientific collaborator, Dr. Siedentopf, has at the instance of Zsigmondy worked out independently an idea previously conceived by Abbe, into a method which makes it possible to see minute particles by means of intense illumination."

As this statement can easily lead to a misunderstanding that the idea conceived of by Abbe was known to Siedentopf or myself, it must be expressly stated that on the occasion of the conversation which preceded the support of our work by the firm of Zeiss, Professor Abbe made no mention of this idea, and that it is unknown to me when and where Abbe has expressed such an idea. Some verbal expression of opinion is probably referred to, which was not available to a wider circle.

CHAPTER V

DESCRIPTION OF THE APPARATUS FOR MAKING VISIBLE ULTRAMICROSCOPIC PARTICLES

It is easy to see why, with the earlier microscopic methods of observation, the individual particles in colloidal solutions or in ruby glass could not be seen. Transmitted light [1] was mostly used for observations, and the eye dazzled by the profusion of light, could not distinguish the slight differences of brilliancy caused by the diffraction of the light due to very small particles, just as it is impossible to see the stars by daylight.[2]

To render visible very small particles, there are necessary:

1. The most intense possible illumination of the particles, in such wise that no beam of the illumination enters direct the eye of the observer.

2. A field of view as dark as possible.

These requirements were met by the construction of an apparatus for illumination, the description of which by H. Siedentopf,[3] I here repeat. Fig. 2 shows the apparatus $\frac{1}{20}$ natural size.

[1] The so-called dark field illumination, then very incompletely developed, has been relatively little used; I do not therefore need to take it up further.

[2] See the detailed discussion of the principles of making visible ultramicroscopic particles: Sidentopf and Zsigmondy, loc. cit., pp. 2–5, and Siedentopf, Berl. klin. Wochenschr., 1904, No. 32.

[3] Siedentopf and Zsigmondy, loc. cit., p. 8. See also the detailed description of the apparatus for making visible ultramicroscopic particles, by H. Siedentopf, Druckschr.-Verz. der optischen Werkstätte von C. Zeiss, Sign. M., 164, Jena, 1904.

"The solar rays reflected from a heliostat, enter the darkened laboratory through an iris diaphragm. In the room is an optical bench about 1.50 meters (5 ft.) long, having a metal flange *P*, supported on an adjustable stand *G*, all made by C. Zeiss, Jena.

"On this, by means of carefully adjusted brackets, are mounted the individual parts of the apparatus. The

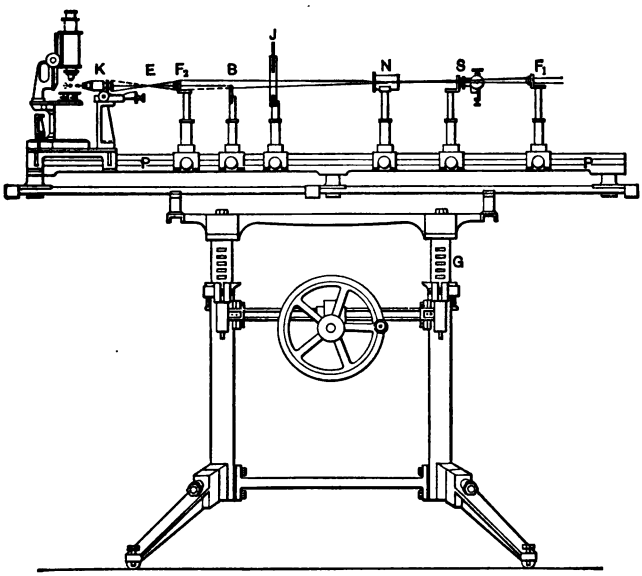


FIG. 2.

light-rays first enter the telescope objective *F*, having a focal length of about 10 mm., which throws an image of the sun about 1 mm. in diameter on the finely adjustable slit head *S*, which is modeled after Engelmann's microspectral-objective.[1] By the horizontal bilateral slit, this image can be reduced to 5–50 hundredths of a milli-

[1] Th. W. Engelmann, Zeitschr. f. wissensch. Mikrosk., 1888, Vol. V, p. 289. H. Siedentopf, Sitzungber, D. k. Akad. d. Wissensch., zu Berlin, 1902, Vol. XXXII, p. 717.

meter, as desired. The width of the slit may be read off from an index on the drum connected with the screw. The edges limiting the height of the slit are movable horizontally, and may be placed from $\frac{1}{10}$ to 2 mm. apart. A polarizer *N* may be placed behind the slit when desired. The iris diaphragm *J* shuts off any side-light which may be reflected from the edges of the slit. By means of the chisel-shaped diaphragm *B*, one-half of the beam of light may be cut off; this is necessary when immersion objectives are used, in order to prevent objectionable reflection from the mounting of the front lens, due to the closeness of the objective. A second telescope objective F_2 of 80 mm. focal length forms a quarter-size image of the slit at the focal plane *E* of the condenser *K*. By means of the microscope objective *AA*,[1] used as a condenser, this picture *E* (reduced to one-ninth its size), is projected into the preparation. It should be seen that full use is made of the aperture of the condenser system *K*, by controlling the illumination of its rear focal plane. The upper half of the rays emerging from the objective *AA* are cut out, when the picture of the semi-diaphragm *B*, thrown by the telescope objective F_2 into the after-focal plane of *AA*, darkens the upper half of this plane. By means of two micrometer screws, working in a horizontal plane and perpendicularly to each other, the condenser-objective may be readily centered in the optical axis of the microscope proper."

In order to bring the desired part of a solid preparation into the axis of the illuminating beam, Siedentopf devised a metal prism having slides permitting the vertical micrometric motion of a little plane table.

For the examination of fluids I had made a small washable apparatus illustrated in Fig. 3, which makes it

[1] *AA* is the mark on the Zeiss objective referred to.

possible to examine numerous fluids, one after the other, without being obliged to rearrange the microscope for each case.

A cell with a quartz window *C*, which serves as observation chamber, is connected by tubes on the one side with the thistle-tube *T* for filling, and on the other side with the pinch-cock *H* for drawing off. In a few seconds one fluid can be run off and replaced by another after washing the apparatus, which remains ready in place for the next observation.

H. Siedentopf has very cleverly attached this little

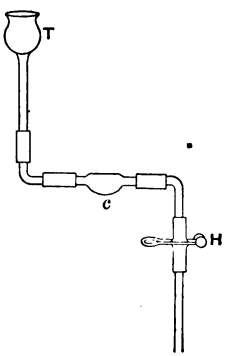


FIG. 3.

apparatus direct to the objective of the microscope, thus obviating the necessity of repeated focusing on one object plane; and the fine adjustment of the microscope tube may be used to move the cell vertically.

Recently W. Biltz proposed a slight modification of this apparatus. In order to avoid the rubber tube connections Biltz fused a thistle-tube direct on to the cell. The danger of increased fragility has been avoided by H. Siedentopf, who made appropriate changes in the cell and the method of fastening it to the microscope objective. The manner of handling the new apparatus is

shown in Fig. 4. The cell, as a whole, is placed in a pocket under the microscope, and held there by the clips *d*, *h*, and *s*.

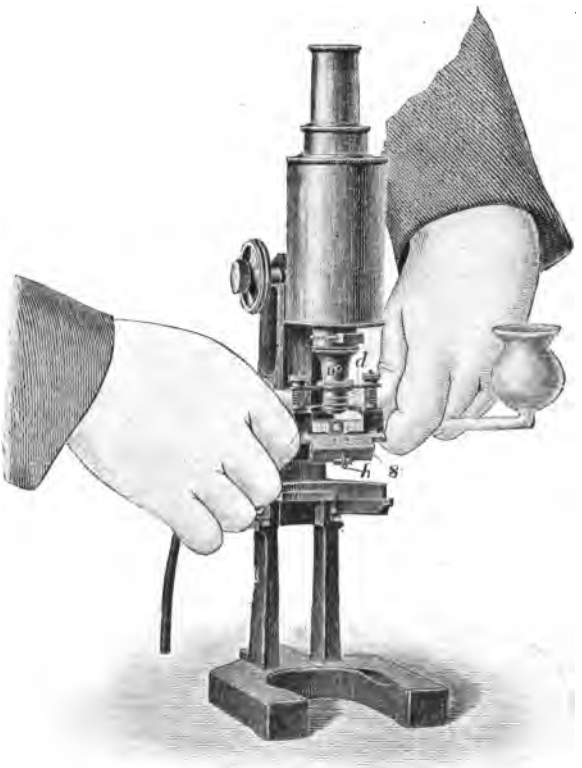


FIG. 4.

H. Siedentopf has also constructed a microscope for the examination of ultramicroscopic bacteria, which has a new arrangement for illumination, entirely different from the one here described.[1]

[1] H. Siedentopf, loc. cit., Chapter IV, and Journal of the Royal Microscopical Society, 1903, pp. 573–578.

Another arrangement preventing the rays in ultramicroscopic work from entering the microscope proper by total reflection from the cover-glass, has been described by Cotton and Mouton.[1]

[1] Cotton and Mouton, Comp. rend., June 1903, Vol. CXXXVI, pp. 1657–59.

A detailed description with directions for the use of the ultramicroscope and its attachments, is issued in English and in German by the makers of the instrument, C. Zeiss, Jena, and may be had by writing for the catalogs known as Micros 227, 228, 229.

The observance of two precautions will save much time for beginners:

1. Be sure the substance examined contains particles that can be rendered visible by the illumination used.

2. Avoid vibration of the instrument, especially when examining fluids.

J. A.

CHAPTER VI

CERTAIN TERMS OFTEN USED HEREIN

E. von Behring has proposed to call the herein described apparatus for rendering visible ultramicroscopic particles, "Ultraapparatus" for short, and to designate as "Ultramicroscope" the microscope constructed by H. Siedentopf for the examination of bacteria.[1] The preliminary research was carried out exclusively with the first apparatus referred to above; and the name proposed by von Behring will be often used. I must observe, however, that other investigators[2] use the name "Ultramicroscope" for the instrument termed by von Behring "Ultraapparatus." It is therefore advisable to keep the expression Ultramicroscope for both kinds of apparatus, and in case it is necessary to distinguish between them, to call the former Ultraapparatus, and find some short name for the latter.

H. Siedentopf has also proposed to establish a further classification of the so-called ultramicroscopic particles.[3] He terms ultramicroscopic a particle or dimension which is below the limit of microscopic resolvability (in practice about $\frac{1}{4}$ μ). According as the ultramicroscopic particle can be rendered visible or not, it is designated as

[1] H. Siedentopf, see note 3, p. 103.

[2] Raehlmann, Zeitschr. f. ärztl. Fortbildung, 1904, No. 5. W. Biltz, Göttinger Nachr., 1904, No. 4.

[3] H. Siedentopf, Berlin klin. Wochenschr., 1904, No. 32.

"submicroscopic" or "amicroscopic." These terms will often be used here.

In order to avoid continual use of the term "particles," I will introduce an additional simplification, and amplifying Siedentopf's proposed nomenclature, I shall call ultramicroscopic particles "ultramicrons," the submicroscopic particles "submicrons," or "hypomicrons," and the amicroscopic particles "amicrons."

CHAPTER VII

PRINCIPLES OF THE ULTRAMICROSCOPIC INVESTIGATION OF FLUIDS

The manipulation of the glass apparatus, for the examination of fluids, illustrated in Fig. 3, is very simple. The microscope tube is taken out from the stand, the space between the objective and the upper quartz surface of the cell is covered with the immersion fluid (in the case of objective *D** with water, which may be squirted between the objective and the cell from a wash bottle), after which the quartz window in front is dried with a clean linen cloth. The funnel is then filled with a turbid fluid (diluted milk, a solution of gum gamboge, commercial colloidal silver, etc.), the pinch-cock *H* (Fig. 3) is opened until all air is expelled from the apparatus, which is sometimes effected by tapping or holding the tube slanting.[1] Then the tube, together with the objective and the washable apparatus attached to it, is again slid into the stand; the microscope proper is moved so as to bring within the field of view the apex of the illuminated cone (which can be easily found in the turbid fluid), and care is taken that the narrowest constriction of the cone is brought to the center of the field.[2]

[1] Good cells fill up at once with the fluid and retain no air bubbles; the turbid fluid must be greatly diluted.

[2] Beginners will best learn the necessary manipulation by practice. Before using the apparatus it is necessary to see that the glass tubes connected by rubber tubing approach each other closely.

When the apparatus is adjusted, the fluid used for this purpose is run off by opening the pinch-cock *H* (Fig. 3), and the cell rinsed out with water until all turbidity-producing particles are removed; the apparatus is then filled with the fluid to be examined, the first portion of it, in quantitative determinations, being used to wash out the water.

I will now take up the description of examinations of a general character, and will begin with distilled water.

1. Distilled Water

As Spring has found, distilled water is not optically clear; it can be freed from the last traces of suspended or colloidally dissolved substances only by somewhat complicated operations. It is evident, therefore, that these impurities prejudice the use of ordinary distilled water in ultramicroscopic investigations to such a degree that it cannot be used to dissolve colloids, or to dilute colloidal solutions. From experience, however, it has been learned that in the case of water which stood long enough protected from dust, the dust particles are present in relatively small number, so that only a few of them come into the field of view, and the space actually under observation is for the most part free of them. The use of such water for many investigations, therefore, seems permissible.[1] In between the suspended dust particles which float perfectly quietly, the water either appears

[1] Stirring with glass rods and taking water from squirt-bottles, should both be avoided. Water is best drawn from a fixed vessel whose siphon tube does not reach the bottom, into a beaker previously rinsed out, and from this it can be poured into the thistle tube of the apparatus. It is advisable to set up several fixed vessels. The siphon is closed with a rubber tube and a pinch-cock. (See also the suggestions of Biltz and Gahl, mentioned in Chapter XX of this book.)

optically clear, or shows upon further opening the slit (whereby a light-cone of greater depth is seen) a weak, diffused shimmering of light, due to traces of colloidally dissolved substance,[1] which do not disturb ordinary investigations, where a narrow opening of the slit is necessary.

In further prefecting the method, and in the examination of fluids whose particles approach the limit of visibility, there should of course be used only water which shows no light-cone in the ultraapparatus. By double distillation and prolonged standing water can be obtained that is suitable for refined work; in which case dust must be excluded as far as is possible.

Recently W. Biltz has published a very good method for the production of clean water (see Chapter XX).

2. Colloidal Solutions

In colloidal solutions the microscopic form of the light-cone is distinctly different from that of distilled water. The distance between the particles in them is usually less than $\frac{1}{4}\ \mu$, and in such cases there appears a more or less intense homogeneous polarized light-cone; very often larger particles are present which shine brighter and give the light-cone a heterogeneous appearance. In order to form an idea as to the individual particles, extreme dilution (0.001–0.0001 per cent and less) is almost always necessary; then only does the distance between the particles become so great that its microscopic resolution is possible.

If the light diffracted from the individual particles is intense enough to create an impression on the retina,

[1] Probably of silicates from the glass or of metal oxids from the cooling tube.

the microscopic pictures of the particles will appear as little reflecting disks; in the case of submicrons, with the most favorable illumination, this is always the case. If the diffracted light is too weak, the light-cone will gradually vanish with increasing dilution, and there is no optical resolution, the solution in such cases containing amicrons.

It is very important to distinguish the casual, suspended particles which, especially in concentrated solutions, are often present in large numbers, from the regular constituents of colloidal solutions. This can be accomplished by extreme dilution; the spaces between the suspended particles then become so large that the light-cone which lies between them and is produced by the smaller particles, can easily be recognized. Upon still further dilution there is re-solution into individual particles (submicrons), or else the light-cone vanishes (amicrons). In the latter case the presence of extremely finely divided substance can be demonstrated by the addition of optically clear precipitants.[1] By such addition the colloidally dissolved particles can be forced to combine into larger ones, which frequently, then thickly fill the field.

In this manner I demonstrated the presence of colloidal gold and of albumen in almost homogeneous solutions.

Those who later enter on this field of work will do well always to make such a test, for the uninitiated are very apt to be deceived by large particles, especially in the examination of concentrated solutions.[2]

[1] Sometimes by boiling the fluid, as for example with albumen.

[2] In dilution experiments it is to be observed in addition, that distilled water sometimes precipitates individual colloids, globulin for instance being precipitated by water. In such cases instead of water a

Polarization. Tyndall has already shown that light is polarized by particles which are very small as compared with its wave-length, whereas by larger particles this effect is produced only partially, or not at all. In connection with Rayleigh's theory, these facts were often investigated and Tyndall's observations confirmed.[1]

I might here make mention of an observation which may seem very strange with reference to the foregoing, but which has been repeatedly confirmed in the case of colloids; there are particles floating in the fluid, which, notwithstanding their relatively large size as compared with the wave-length of light, totally polarize it, and can therefore be rendered invisible by turning the Nicol. Particles of this kind I have observed, for instance, upon the precipitation of a dilute solution of $CuSO_4$ by Na_2CO_3; the light diffusely scattered by the precipitated hydrogel of copper carbonate proved to be polarized, even if the flocks were so large that they could be seen with the naked eye.

The same is the case with colloidal ferric oxid; its solutions, as well as its flocculent precipitate, plane polarize a beam of light in the same direction.

This phenomenon appears to be quite common, and shows itself as soon as hydrogel particles float in the fluid, no matter whether they are large or small as compared with the wave-length of light. This is no exception to the rule of Tyndall, above mentioned, which

diluent must be chosen which exerts no precipitative action on the ultramicrons, providing it is desired to obtain the particles in their original condition. In other cases increasing dilution may work disruptively upon the individual particles, by transformation into crystalline solution, for example. Cases of this kind have not yet been carefully investigated.

[1] See for instance B. Pernter, Wiener Denkschriften der Akademie der Wissenschaften, 1901, Vol. LXXIII.

refers to little drops of fluid in steam-clouds, and also to such emulsions as the turbid mastic solution, the polarization of which was closely investigated by Pernter, who among other things concluded "that the *presence* of larger particles involves a *decrease* of the polarization, in proportion to the size and number of such particles present." [1]

The hydrogel particles must, however, be conceived as being thoroughly permeated with fluid. According to Bütschli, hydrogels possess a fine, web-like structure, or according to Quincke, they consist of foam-cells, or foam-chambers with invisible walls. Some such structure, but much finer and perhaps otherwise constituted, must be assumed in the case of each hydrogel particle, even if it is smaller than a wave-length of light, that is so small that the examination of its structure is no longer possible.

Returning to the ultramicroscopic examination of gel particles, a striking difference is at once evident between such an examination and that with the naked eye.

While the rays diffracted by the flocculated particles of the Fe_2O_3 hydrogel, when macroscopically observed, do not appear much brighter than those of the light-cone in the original hydrosol, and can be almost completely blotted out by turning the plane of polarization of the Nicol prism, there can, however, upon ultramicroscopic examination of the same fluid, be seen in addition to numerous small particles, dazzlingly bright larger particles whose light, although weakened, cannot be entirely blotted out by any position of the Nicol prism. On the other hand the less brilliant particles partially or completely disappear with crossed Nicols, sometimes even if they have reached considerable size.

An explanation of this phenomenon I will not here

[1] Loc. cit., p. 11 (p. 310).

attempt, but will merely call attention to the fact that practically no inference as to the size of hydrogel particles can be drawn from the degree of polarization. For a determination of their size, or more properly the mass of the colloid-substance contained in them, recourse should be had to methods which will soon hereafter be described.

Color. Ultramicroscopic particles are usually colored, the color of their tiny reflecting disks, when the particles are alike, being nearly complementary to the color of the mass of the fluid by transmitted light, as has already been mentioned.[1]

So far as our present experience goes this relation is general; it indicates—in harmony with the behavior of turbid media—that the color of the fluid is produced by the preferential separation from the impinging beam of light, of those component rays which are scattered by the individual particles. It would seem reasonable to extend this view to the rays scattered by the molecules of dye-stuff solutions, but such an hypothesis is palpably incapable of demonstration because of the extreme weakness of the diffraction in particles of such small mass.

In order to get a correct idea of the color of the individual particles, it is quite evidently necessary to dilute the fluid until a disk one quarter centimeter[2] thick is practically colorless.

3. Determination of the Size of Particles

In the paper [3] frequently before referred to, two methods were described in detail for the determination of the size

[1] Siedentopf and Zsigmondy, loc. cit.

[2] The approximate length of the path of the light beam in the fluid.

[3] Siedentopf and Zsigmondy, loc. cit., pp. 16–29.

of ultramicroscopic particles. It was there pointed out that these methods give only the average mass of the individual particles, according to the formula $\frac{A}{n}$, where A is the mass of the substance subdivided, and n is the number of particles in it.

For the purpose of tabulation in the case of gold ruby-glass, the average linear dimension l of the individual particles was figured out on the assumption that the gold particles are cubical [1] and are of solid gold, having a specific gravity $s=20$,[2] that is, according to the formula

$$l=\sqrt[3]{\frac{A}{s \cdot n}}.$$

First Method. According to this method a certain illuminated volume of glass or of fluid (V) is blocked out,

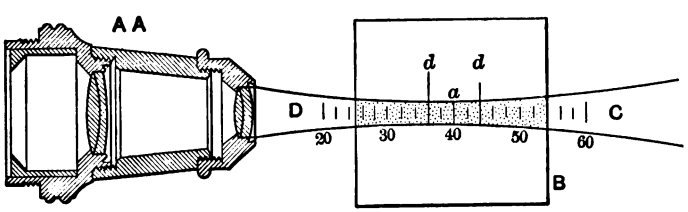


FIG. 5.

the size of this volume determined, and the particles contained in it counted. By means of the eye-piece micrometer a part of the cone of rays *dd* (see Fig. 5), may be sharply defined from side to side, whereby the length and breadth of the volume chosen may be known.

[1] That this assumption is not quite accurate is brought out on p. 36 of the paper quoted. Regarding the detailed discussion of sources of error, I refer to pp. 21–29 of the same paper.

[2] Rose found the specific gravity of precipitated gold to be 19.55 to 20.7.

The depth of the illuminated volume V[1] thus defined may be easily determined with the eye-piece micrometer upon the quarter (90°) of rotation of the graduated slit S (see Fig. 2, Chapter V).

The mass A of the subdivided substance contained in the volume, is found directly from the concentration, providing the total mass of the subdivided body is present in the form of ultramicroscopic particles, as in many colloidal gold solutions. When, however, one part of the subdivided substance is in homogeneous solution (α), and another part is present in the form of submicroscopic particles (β), then since β is unknown, we take, in place of the latter the sum ($\alpha+\beta$), and thus obtain a major limit for the size of the particles.[2]

For full details for the determination of volume, as well as for the sources of error in this method, I may refer to the original article, merely remarking here that in exact determinations of the size of the particles, the error does not exceed twenty per cent of the linear dimension, and is usually considerably less.

Second Method. From the distance between the particles, and using the same assumption, the linear dimension l may be obtained by means of the formula

$$l=\sqrt[3]{\frac{A}{s}}\cdot r,$$

where r is the mean distance between the particles.

[1] For particulars see pp. 17, 21, and 22 of the paper referred to. It will be seen that the depth of the illuminated volume thus determined can enter the calculation only if it is less than the depth of view of the microscope.

[2] Sometimes β can be indirectly determined, as in the case of gold ruby glass, where we can determine β by colorimetry. The major limit is not much different from the actual size of the particles, provided that α does not constitute the bulk of the substance present.

In using this method it should be carefully noted that the mean distance between the particles can be correctly measured only when the depth of the layer under observation is at least as large as this mean distance. The depth of the layer in question must therefore be exactly determined; for if this be not done, or if it is impossible, apparent distances are obtained which may sometimes differ in no small degree from the actual distances.

As mentioned in the paper above referred to,[1] the measurement of the distance between the particles in the case of fluids is made very difficult by their motion; numerous measurements must therefore be made on one and the same fluid in order to obtain an average of practical value. The probable accuracy of the results obtained is considerably increased, if various degrees of dilution are examined.

In the case of colloidal gold solutions I have for the most part worked as follows: Each fluid to be investigated was first reduced to a content of 0.005 per cent of metallic gold, and when possible, the first series of counts made with this. Thereafter the hydrosol was diluted 8, 27, 125 times, or 10, 100, some times even 1000 times, and at each dilution the measurement of the distance between the particles again repeated. The mean of all the figures was taken, and from this was calculated the distance between the particles in the original concentration; and as a control of the value thus obtained, in many instances the number of particles contained in a given volume was determined by the first method.

First Method Applied to Fluids. As the particles are in continuous motion, it is not possible to count off a large number of them; it is therefore necessary to so limit the volume of the fluid illuminated, or so dilute a

[1] Siedentopf and Zsigmondy, loc. cit., p. 29.

given volume of the fluid, that on the average about from 2–5 particles are contained therein, which number may be determined at a glance.

By frequent repetition of this same procedure in different parts of the fluid, and with various degrees of dilution, there may be obtained a pretty good average value of the number of particles in a certain volume, which thus serves to control the value obtained by the other method.[1]

The results of neither method, of course, have any great degree of accuracy, but they both satisfactorily serve the purpose of this book—to establish some kind of order in a field hitherto inaccessible to direct observation. The brightness of the diffracting disks also furnishes a good control for the size of the particles, because

[1] With fluids which contain a variety of different sized particles, it is evident that the number of particles in a given volume will not be found proportional to the concentration of the colloidally dissolved substance, but that in the more concentrated ones it is too small. For example, with a silver hydrosol (Bredig's method) I obtained, as an average of about 20 separate measurements with a concentration, C=0.0037 per cent:

	Concentration in 440 μ^3		Calculated to concentration C
C	3.50	particles	3.50
C/2	2.28	"	4.56
C/4	1.95	"	7.80
C/8	1.62	"	12.90

Upon greater dilution many more particles are therefore counted than with greater concentration, and the reason of this is chiefly because the smaller particles become distinctly visible only when by great dilution the larger particles are in part removed from the field of view.

The average linear dimension, according to the first count was, found to be too large in the proportion of $\sqrt[3]{12.9} : \sqrt[3]{3.5}$, that is about 1.5 times greater than by the last count. In such cases it will be better to report, not the average value, but the superior limit determined by various degrees of dilution.

in general those particles of a certain substance which have been determined to be the largest, must naturally diffract most light. The brightness and color of the diffraction-pictures, as well as their motion, are such characteristic features of the particles that it is easy, in a mixture of two fluids of different properties, to determine by ultramicroscopic observation of the particles, which belong to one fluid and which to the other.

The results of the series of investigations hereafter given, thus mutually support each other.

In addition it may here be stated that gold particles whose linear dimension was found to be 15 $\mu\mu$ (15.10^{-6} mm.), lie at the limit of visibility with illumination by the electric arc,[1] and that smaller particles can be discerned only by the use of sunlight; while the smallest that can as yet be rendered visible, which are about as small as 5 $\mu\mu$, can be seen only with the brightest sunlight on very clear days and with efficient means for cutting off all extraneous light.

As the index of refraction of metallic gold is very different from that of water, and this difference is favorable for rendering visible ultramicroscopic particles, it stands to reason that particles of other substances which are smaller than 15 $\mu\mu$ cannot be made visible by arc-light with the present apparatus, excepting those of some few metals and perhaps those of fluorescent dye-stuffs.

I am obliged to state this here, because many divergent statements have been made by others about the limits of visibility of ultramicroscopic particles, and such state-

[1] This statement refers to our apparatus ordinarily used for examining fluids (objective AA [num. ap. = 1/3] for illumination, and objective D * [num. ap. = 3/4] for observation). According to Siedentopf the brightness of the diffraction disks is proportionate to square of the product of the numerical apertures of the objectives used for illumination and observation.

ments might easily lead to an exaggerated idea of the method described by Siedentopf and myself. Without further remarks, it follows from what has been said that when colored particles are observed with the ultramicroscope in the solutions of dye-stuffs like acid fuchsin, naphthol yellow, etc., which dissolve as electrolytes, these particles cannot be molecules or ions of the dye-stuff in question, that is, they cannot be its smallest particles.

CHAPTER VIII

PREPARATION OF COLLOIDAL GOLD SOLUTIONS

THE gold hydrosols used for the experiments hereafter described, were prepared by two different methods.

One I have described in Liebig's "Annallen," Vol. 301, p. 30; the other will be given here.

First Method. A dilute solution of chlorid of gold is mixed with potassium carbonate and reduced at the boiling-point by formaldehyde. If bright red clear fluids are desired, which can be used as colloid reagents, the details described in the "Zeitschrift für Analytische Chemie"[1] must be exactly followed.

The chief essential is distilled water of sufficient purity. The absence of electrolytes is not so essential as the absence of colloids; traces of the former do no harm, seeing that a certain quantity of them is introduced into the water by the reagents themselves. On the other hand traces of colloids almost always present in all *commercial* distilled water completely prevent the formation of bright red gold hydrosols. With such water there are usually obtained blue, violet, purplish suspensions which, in a few days or weeks, deposit the greater part of their gold.

For this reason I gave directions to redistil the distilled water, using a silver worm for condensation.[2]

[1] Zeitschr. f. analyt. Chem., 1901, Vol. XL, p. 710.

[2] I often obtained bright red fluids by using frozen water, and once

Some impurities which I have found particularly injurious are: Phosphates of the alkaline earths, silicates from the glass itself, colloidally dissolved substances originating from the cooling worms ordinarily used, organic substances in commercial distilled water, and others of like kind.

It is not difficult to see how these impurities act. The colloidally dissolved substances permeate the entire water, and in spite of their very small quantity are so thoroughly distributed that the distances between their particles are for the most part beyond the resolving power of the microscope. Therefore, as above described, they appear upon ultramicroscopic observation as an extremely faint homogeneous, polarized light-cone, which encloses much larger dust particles. The finest dust of Konowalow's [1] fluids, which according to the publications of this investigator play an important rôle in the turbidity of critical solutions, may, in so far as aqueous fluids are concerned, be the same as the colloidal impurities here described.

The mutual precipitation of colloids makes possible the formation of large particles capable of producing turbidity. As Picton and Linder,[2] Lottermoser,[3] and recently W. Biltz [4] have shown, colloid solutions with oppositely conducted particles mutually precipitate each other. When therefore reduced gold and the colloidal

even by using water condensed in a tin cooler, but in any event only after prolonged distillation. The same was observed by W. Biltz, Göttinger Nachr. 1904, No. I.

[1] Konowalow, Drude's Ann., 1903, Vol. X, pp. 360–392 and also Vol. XII, pp. 1160–64. The term "finest dust" is perhaps not a happy one, for ordinary dust particles are as a rule incomparably larger.

[2] Loc. cit.

[3] Ueber anorganische Kolloide, Stuttgart, 1901.

[4] Berichte, 1905, Vol. XXXVII, pp. 1095–1116.

impurities are oppositely conducted, there is a possibility that a coarse turbidity may be found.[1]

Other conditions may enter, but to discuss them would lead us too far.

By the use of sufficiently pure water a quantitative reduction of gold may be obtained with formaldehyde in fluids which contain only 0.00005 per cent of gold, that is, one hundred less times gold than the bright red ones, and the fluids thus obtained may be evaporated without decomposition to one-fiftieth (1-50) of their volume, and still further. In such fluids the gold is amicroscopic, that is, in particles so small that they cannot be made visible.

The second method for preparing almost homogeneous gold solutions may be regarded as a combination of my method with that of Faraday. This method has the advantage of making it relatively easy to obtain the

[1] Recently Jordis (Zeitschr. f. Electrochem., 1904, p. 510) has advanced the opinion that the impurities dissolved in water are necessary, as "sol-formers," to the formation of colloidal metals. Upon the basis of his observations on silica and also the observations of Lobry de Bruyn and Paal, Jordis infers that it is easier to obtain more concentrated solutions of colloidal gold in the presence of certain organic substances (protective colloids) than without them. It should not be overlooked that the colloids of Lobry de Bruyn and Paal are analogous to the purple of Cassius, showing a much different behavior with reagents and upon desiccation than the colloidal gold made by Bredig's method or my own, and being subject to different conditions of formation. To this I shall later return. A protective colloid would by all means facilitate the production of colloidal gold and act as a "sol-former"; the impurities contained in water, however, generally have the opposite action, and are not "sol-formers," but sol-destroyers. Therefore the advice to work with purest water possible. The addition of alkali or alkali carbonate produces, as Bredig has shown, a decrease in the concentration of the hydrogen ions, which also militate against the formation of metal hydrosols, or an increase in the concentration of hydroxyl ions which are favorable to the formation of gold hydrosols (see also pp. 64 and 77–79).

finest subdivisions even in more concentrated solutions (0.005 per cent Au).

I use in exactly the same concentration the same mixture as with reduction by formaldehyde, but instead of heating with formal, reduce at room temperature with a few drops of an ethereal solution of phosphorus.[1] (Proportions 120 cc. water condensed in a silver cooler, 15 mg. $AuHCl_4 . 3H_2O$, 37 mg. K_2CO_3). Here, as in the other method, the use of colloid-free water is essential. The formation of the hydrosol takes place slowly, the fluid first becoming bright brownish red, and then gradually bright red, often with a tinge of brown-red, without showing the slightest turbidity to transmitted or reflected light.

If a good solution has been prepared,[2] it can be seen, upon testing with a lens and sunlight, that in it diffuse dispersion is almost entirely lacking, and that it is almost indistinguishable from a mixture of the reagents without gold. Ultramicroscopically there may be seen in it a few gilded dust particles, and among them an unresolvable, extremely faint light-cone, which soon disappears upon diluting the fluid with the purest kind of water, no individual particles being discernible.

This fluid stands boiling without alteration, in contradistinction to that prepared by Faraday, which was thereby rendered turbid, and deposited its gold.

The contamination of 120 cc. of the purest water (condensed in a silver cooler) with a few drops of water in which had been stirred up some powdered glass, or the

[1] It is best to take about one-half cubic centimeter of an ethereal solution of phosphorus, made by diluting a concentrated solution with five times its volume of ether.

[2] From a larger number of separately prepared fluids the best must be selected in order to obtain fluids of the greatest homogeneity.

use of commercial distilled water for the preparation of the gold solution, yielded sometimes very turbid fluids, which, like Faraday's, become violet and settle upon boiling, instead of being nearly homogeneous.[1]

The influence upon the reduction of gold of the colloidal impurities in distilled water was not known to Faraday;[2] he obtained, therefore, upon reduction with phosphorus, a variety of fluids, mostly suspensions which settled soon after their preparation, but sometimes stable colloidal solutions, which, however, would not stand boiling.

Third Method. Proceed as in the first method, but shortly before the addition of the formaldehyde add to the 120 cc. of water from 0.5 to 4 cc. of the nearly homogeneous gold solution produced according to the second method. The tiny gold particles act as nuclei (see Chapter XVII, 3), and grow in the reducing mixture. According to the quantity of gold fluid added, there are obtained gold solutions with larger or smaller particles.[3]

[1] In these experiments no alkali carbonate was added.

[2] He also knew nothing of the beneficial influence of the addition of alkali carbonates on the formation of finer subdivisions (for the purpose of neutralizing the acid formed.) Nevertheless very profound subdivisions may be obtained with phosphorous without K_2CO_3, providing the other conditions are observed. The age of the phosphorous solution used and its degree of dilution also influence the properties of the gold solution.

[3] Zsigmondy, Z. phys. Chem., Vol. LVI, p. 65 (1906).

CHAPTER IX

ULTRAMICROSCOPIC EXAMINATION OF THE SOLUTIONS OF GOLD

THE figures given in the following table are the result of a very careful investigation. Apart from the fact that the work was several times interrupted and taken up again, it was further complicated because for the most part I needed direct, bright sunlight, which is somewhat rare in Jena; it often happened that just when all the preparations for an examination had been made, a cloud would pass before the sun.

The hydrosol Au_{97} was most thoroughly investigated, an average value being obtained based upon more than three hundred individual measurements made in collaboration with Dr. F. Kirchner on three different concentrations.

We found as the average value of the distance *between the particles:*

	Distance Observed.	Distance Calculated for Undiluted Fluid.
With undiluted fluid	0.972 μ	
Upon dilution, 1:8	2.33 μ	1.16 μ
Upon dilution, 1:125	5.67 μ	1.13 μ

Average of combined observations 1.13 μ.
Size of particles calculated therefrom 15.25 $\mu\mu$.

The values for the sizes of particles in fluids which were less carefully examined, will show considerably

greater variation from the true mean, the error in some cases being perhaps thirty per cent. There is great uncertainty in the values for fluids about the limit of visibility. On the other hand the accuracy of the results are strongly supported by the practice which the eye gets in estimating the size of the particles from the brightness of the diffraction-images.[1]

As often previously stated, our method yields only an average value for *the mass of the particles;* to make comparison convenient, the linear dimensions were calculated therefrom as before, on the assumption that the particles are cubical and completely filled with metallic gold. I must, however, expressly caution against assuming that this imaginary cubical or globular form corresponds with the actual fact; many observations indicate that never, or only in isolated cases, do the metal particles have a similar shape on all sides. To this subject I shall later return.

In the first column of the following table are given the names of gold solutions, AuP designating the solution obtained with phosphorus by the second method, while Au_{73}, Au_{101}, etc., designate those obtained by the first method. With the exception of Au_{73} and Au_{73a}, which were reduced from a 0.0005 per cent solution of gold chlorid, all the other liquids when they were made contained from 0.005 to 0.006 per cent of gold. For the purposes of examination they were diluted to 0.005 per cent Au, and fractions of this percentage.

In the second and third columns are given the colors of the particles and the fluid, and when no individual particles were visible, that of the light-cone.

The length of the path described by the submicro-

[1] As has been brought out in Drude's Ann., Vol. X, p. 29, the differences in brilliancy are extremely great.

scopic particles, designated by *A* in column V, serves merely for a preliminary orientation. The motion of translation is made conspicuous, while the much smaller motion of oscillation, to which every particle is subjected, is not given. As a rule—not without exception—it may be stated that the motion is more rapid the smaller the particles and the greater the number contained in unit volume. Upon dilution, therefore, the activity of the motion decreases somewhat.

Very large particles of gold and gilded dust particles float, for the most part, quietly in the diluted fluid; in concentrated ones they are sometimes struck by the smaller particles, thus acquiring motion.

In the table the fluids are arranged according to the size of the particles.

Glancing at the table, there is seen at the top a very interesting fluid: AuP_{16}. When just made, this is bright red, and completely clear both to reflected and transmitted light. The gold in it is subdivided to a degree approaching homogeneity, for outside of coarse yellow particles about 0.05 mm. apart (probably gilded dust), hardly a trace can be seen of the bulk of the gold, even in the ultraapparatus.

The milliards of individual particles which fill every drop of the other fluids (for instance Au_{97} or Au_{101}) are here completely lacking, or more correctly, they escape observation on account of their small size. Their ability to diffract light has become so reduced that even in their totality, they do not diffract more light than is absorbed by the colored fluid, so that it is doubtful if any light-cone due to gold particles in the solution can be seen at all. That this is a colloidal solution of metallic gold, and not some red chemical compound of gold, can at once be proven by the addition of electrolytes. As the experi-

ment in the second section of the table shows, the well-known color-change to blue then takes place, and the light-cone—due to gold particles—then becomes visible. (For more in this connection see Chapter XII.) That reduction with phosphorus yields the metal, Faraday[1] has already shown. I have repeatedly tested the fluid AuP, and have reached the conclusion that, if my instructions are adhered to, almost homogeneous gold solutions can be obtained. By reducing the gold with formaldehyde, I obtained, as already mentioned, similar fine subdivisions only when I had at my disposal water of especially good quality, and diluted the gold chlorid solution before reduction to from eighty to one hundred times its usual concentration, that is down to about 0.000005 per cent of gold.

Between the finest subdivisions of gold just described, and those whose particles just become visible under most favorable conditions (Au_{73a}, line 7), there are a whole series of transition forms which can at present be produced, but whose detailed description would carry us too far.

Upon examining the fluids in order of the size of their particles, there are seen in the ultraapparatus, with increasing size, the following phenomena: the light-cone is hardly discernible (line 1, AuP_{16}); it becomes more distinct and brighter (line 3), but vanishes upon dilution; the color of the light-cone may be recognized (lines 4–6), it becomes still brighter, and acquires a heterogeneous appearance, but the individual particles are still amicroscopic (Au_{73}); upon sufficient dilution and with the brightest sunlight the individual particles become visible

[1] Phil. Trans. of the Roy. Soc. of London, 1857, Vol. CXLVII, p. 163.

[2] Slight deviations from the directions may result in very turbid fluids.

VI. Date of Preparation.	VII. Date of Observation.	Remarks.
.....	March 13, 1902	Single yellow particles 40–50μ apart, with no light-cone visible between them, or at most

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(smallest submicrons, in fluid Au_{73a}, for example); the individual particles then become visible even by arc-light (line 10 and the following). The particles become brighter and brighter, and shine with various colors (lines 14–20), their activity decreases; finally, they become so large that they sink to the bottom (lines 21, 22); they must, however, be still larger in order to be seen in the microscope with ordinary illumination.

CHAPTER X

MOTION OF THE GOLD PARTICLES

As but few have as yet seen the motion of the smallest particles *approaching the limit of visibility with sunlight,* a few remarks on this subject are not out of place.[1]

I here repeat the description which I had written for my Würzburg lecture under the inexpressible impression of the first view of this rare phenomenon, a description of which I had stricken from the manuscript because, on re-reading it at that time, it seemed exaggerated. I had pointed out that large suspended gold particles float quietly in the fluid and sink slowly to the bottom, or else show only an unimportant Brownian movement, and that by conceiving colloidal solutions as suspensions, one would naturally imagine that the gold particles in these too would be as quiet as those in the real suspensions. I then added the description above referred to:

"How entirely erroneous was this idea! The small gold particles no longer float, they move—and that with astonishing rapidity. A swarm of dancing gnats in a sunbeam will give one an idea of the motion of the gold particles in the hydrosol of gold! They hop, dance,

[1] For the demonstration of ultramicroscopic particles with arc light on the occasion of the exhibition of our apparatus at Jena, Berlin, Kassel, and Leipzig, Siedentopf and myself chose for the purpose of distinctness, coarser subdivisions of metals having particles of 20–40 $\mu\mu$.

jump, dash together, and fly away from each other, so that it is difficult in the whirl to get one's bearings.

"This motion gives an indication of the continuous mixing up of the fluid, and it lasts hours, weeks, months, and, if the fluid is stable, even years.

"Sluggish and slow in comparison is the analogous Brownian movement of the larger gold particles in the fluid, which are the transition forms to ordinary gold that settles.

"The smallest particles which can be seen in the hydrosol of gold, show a combined motion, consisting of a motion of translation by which the particle moves from 100 to 1000 times its own diameter in one sixth to one eighth of a second, and a motion of oscillation of a considerably shorter period, because of which the possibility of the presence of a motion of oscillation of a higher frequency and smaller amplitude could not be determined, but is probable."

In Table 5 (page 132), column V, lines 7 and 8, etc., are given in μ the numerical values for the amplitude of the motion of translation, designated by A.[1] At the time of examination hydrosol Au_{92} was over a month old, and hydrosol Au_{73} three quarters of a year old; notwithstanding this they showed the most active motion. Even in still older solutions similar motions were evident, for instance in the fluid Au_{50} (made October 12, 1898, examined April 26, 1901).[2] Frequently—especially in the case of less stable fluids—a decrease in the activity of the motion may be seen in the course of time, probably in connection with the commencement of the coagulation of the solution in question.

[1] See what is said on this subject in Chapter IX, p. 130.

[2] A fluid which had lost the larger part of its gold by being frozen in the winter of 1900.

I must expressly call attention to the fact that this motion of the little gold particles just described, differs in many respects from the typical Brownian movement.[1]

In the following table are arranged some of the data concerning the Brownian movement given by various investigators for comparison with those of the gold particles.[2]

TABLE VI

Kind of Particles.	Diameter in μ.	Free Path in μ.	Observer.
1. Gold (Au_{73})	0.006	over 10	Zsigmondy
2. " (Au_{90})	0.01	3–4, sometimes and over	"
2*a*. " (Au_{70})	0.035	1–7	"
2*b*. Dust particles in distilled water	less than 0.2	imperceptible	"
3. Little spheres	0.5	2.5	Regnauld
4. Gum gamboge	.....	1–2	Zsigmondy
4*a*. " "	.....	1–2	Chr. Wiener
5.	1.1	1.4	Ramsay
6.	4	0	Exner

The free paths referred to in the table are traversed in different times. The little gold particles, as far as may be observed, cover the distance designated, in $\frac{1}{6}$ to $\frac{1}{8}$ of a

[1] Compare this with gum gamboge, Chapter XIX. Atterberg (see note 1, p. 17) found (in harmony with Exner) that sand grains less than 2μ exhibit lively Brownian movement, while grains coarser than 3μ no longer move.

[2] The more lively motion (up to 8μ) observed by Renard in iodin particles and turbid solutions of rosin in water and alcohol, may be explained according to Quincke's idea (Drude's Ann., 1902, Vol. VII, p. 67), as the consequence of the fluid stretching out in the little interstices to the surface of the particles.

second, and even less; larger particles take somewhat longer to traverse their shorter paths.

The speed of the motion of the particles cannot therefore be seen from the table; it is very difficult to observe, although the difference in motion may, however, be clearly recognized. Perhaps more accurate data may be made possible by the cinematograph (instantaneous photography); for the present we must be satisfied to obtain only an approximate picture of the motion. In order to make this idea clearer, there is illustrated in Fig. 1, Plate II, the motion of a gold particle 0.01 μ in diameter,[1] and for comparison the paths and diameters of the other particles referred to in the table, all enlarged 5000 times. And finally, in Fig. 6 is given (according to arbitrary scale), the typical Brownian movement of the fat globules in milk, according to O. Lehmann.[2]

Concerning this motion, Lehmann writes: "Here we may wait in vain for such a drop to come to rest, for it moves continuously, describing an irregular zig-zag line to and fro, vibrating unsteadily about a mean position seldom reached; only when by chance it rests against the side of the vessel, or when several unite to a larger conglomerate, does the motion cease."

In contradistinction to this typical Brownian movement about a mean position, the motion of the little gold particles is continuous, a quick moving gold particle for instance, after a series of speedily

[1] From the great variety of paths observed I select one arbitrarily, so that the diagram has no claim to accuracy.

[2] Lehmann, Molekularphysik, Leipzig, 1888, Vol. I, p. 264. In this book there is also discussed in detail the work of other investigators (up to 1888), from which several dates are taken.

executed zig-zag moves, rushing across the illuminated field of view, almost as if it were a living thing, and vanishing; whereas larger particles may for the most part be conveniently viewed for a long time before the slow current of the fluid removes them from the field of view.

In accord with the observation of Exner, that larger particles show less active Brownian movement than smaller ones, I can also state that in general the motion of the gold particles becomes more sluggish and of greater period with increasing size, and in the case of quite large sized particles sometimes ceases. This latter rule is subject to exceptions, for I sometimes found quite large submicroscopic particles in active motion.

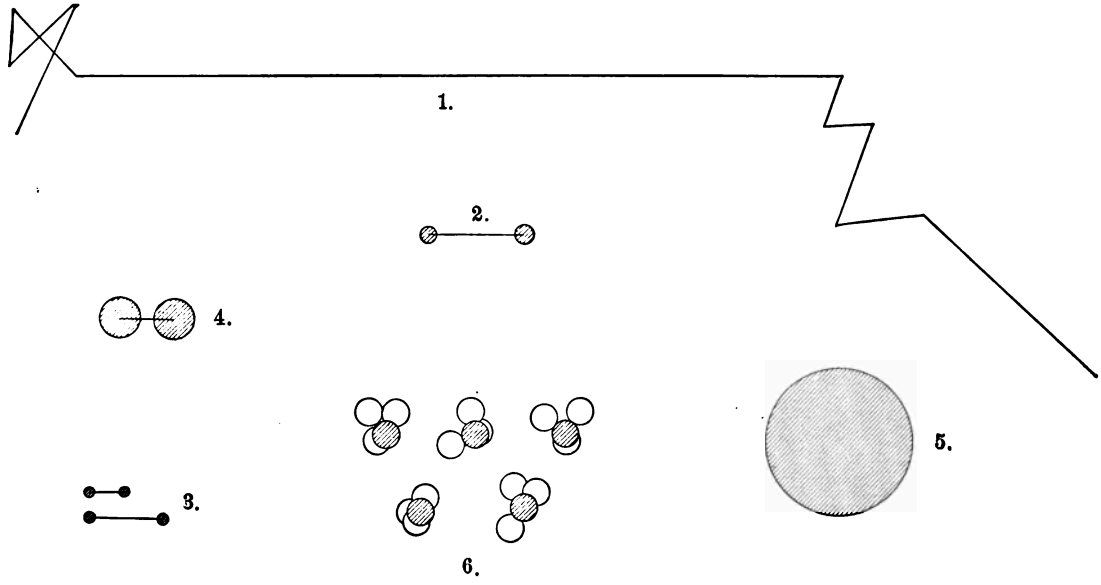
Furthermore, the kind of the subdivided substance (or its surface properties?), appear to influence the motion; thus the ultramicroscopic dust particles of distilled water show no appreciable movement.

Regarding the Cause of the Motion. I must here oppose the natural inference that the warming of the illuminated layer of fluid or a one-sided illumination of the particles might have considerable influence on the motion described. The motion persists even if a water cell be interposed in the path of the rays of light,[1] and it remains unchanged whether a certain part of the fluid be illuminated for a long or a short time.

With the help of a micrometer screw on our apparatus, the light-cone can be moved horizontally. By suddenly turning the screw, I have repeatedly moved the cone

[1] With very bright particles which could be seen in the broader portions of the light-cone, I could see that the motion there was no less active than at the apex of the light cone, where existed the maximum heat and light effect.

PLATE II



Motion of Particles of Various Sizes and Kinds

1. Gold particles 0.01 μ in diameter.
2. Little spheres 0.5 μ in diameter.
3. Particles of gum gamboge.
4. Particles about 1.1 μ in diameter.
5. Particles 4 μ in diameter (without motion).
6. Brownian molecular motion according to O. Lehmann (arbitrary scale)

Linear magnification, 1 : 5000.

[*To face page* 138]

into a distant, hitherto unilluminated portion of the field of view, and found the movement of the gold particles just as lively there as elsewhere, and similarly independent of the direction of the illuminating rays.

In determining the motion of the particles it should be seen:

1. That during the observation the particles are in a space entirely confined, so that there can occur no change of concentration by dilution, etc.;

2. The motion is independent of the direction of the light rays, and independent of the time a given portion of the fluid has been illuminated, and as far as may yet be determined, of the intensity of the illumination;

3. That in general the smaller gold particles exhibit a *much more active* motion than the larger ones; that sometimes larger particles are met with, having active motion;

4. That some of the fluids investigated which showed lively motion, were several months, some even one and one half years old.

5. That the particles appear to influence each other, and that for the most part the activity of the motion is somewhat decreased by the dilution of the gold solution.

In the case of very small gold particles there is a possibility that the continuous motion may be due to a certain extent to the molecules contained in them; I consider more probable, however, the assumption that the electrically charged gold particles enter into an action of interchange with the ions of the fluid and with each other.[1]

[1] Meanwhile The. Svedberg has shown that the motion of the particles is dependent upon their electric charges.

It will require very careful study to elucidate with certainty the cause of this motion. Although the causes of this remarkable phenomenon may be manifold, it is the kinetic theory of fluids which appears to be of prime importance in explaining the motion, which persists uninterruptedly in the fluid for months and years.[1]

[1] These predictions have been most satisfactorily fulfilled. Einstein, and v. Smoluchowsky (Drude's Ann., 1906, Vol. 21, 756–780), worked out the kinetic theory of the Brownian movement; the numerical values of their calculations agree quite well for the most part with the amplitudes of the motion of the particles as directly determined by The Svedberg (Zeit. f. Elektrochem., 1906, pp. 853–860) and Ehrenhaft.

CHAPTER XI

SIZE AND COLOR OF THE PARTICLES

THE table in Chapter IX confirms—in agreement with Faraday—the statement[1] heretofore often made, that there is no recognizable interdependence between the color and size of the gold particles in ruby-glass and those in gold hydrosols, and that therefore no inference as to the size of the particles can be drawn from the nature of the absorption curve of light rays.[2]

AuP_{16} is a bright red fluid whose gold is in almost homogeneous subdivision, while Au_{208a} is a fluid of the same color; both have absorption bands in the green, and contain bright green particles averaging $32\mu\mu$, some larger, some smaller; and on the other hand $Au_{73,\ 92,\ 101}$, etc., are various bright red fluids with green particles about $6\text{–}20\mu\mu$.

Still larger green particles are doubtless contained in

[1] Zsigmondy, Zeitschr. f. Elektrochemie., 1902, No. 36; Siedentopf and Zsigmondy, Drude's Ann., Vol. X, p. 35, and Verhandlungen d. Deutschen physikal Ges., Vol. V, p. 212.

[2] Stoekl and Vanino, and recently Ehrenhaft (Berichte d. Kais. Akad. d. Wiss., Vienna, 1903, Vol. CXII, p. 181) have calculated from the light absorption of gold sols, the size of the particles contained in them. Their conflict with the facts supported by numerous experiments, indicates that the suppositions made by these investigators are not correct. See also the theoretical treatment of the question of optical resonance of finely subdivided metals, by F. Pockels. Physikal. Zeitschr., 1904, Vol. V, No. 6, pp. 152–156.

gold suspension *A*, for the brightly shining green particles sank to the bottom just like the yellow and red ones.

From the above may be seen, as has been previously noted in the case of ruby-glasses,[1] that green gold particles may occur in various sizes. Every red fluid, no matter what the size of its green particles, changes upon the addition of electrolytes to a blue color, and then contains no (or only a few) green particles, but has instead yellow or red ones, which are all larger than the green ones formerly present; and from the finest subdivision AuP_{16} may be obtained extremely small yellow ones, approaching the limit of visibility, whereas the red hydrosols with large green particles yield quite large brightly shining yellow or red particles. It is therefore within our power to produce both red and yellow particles of various sizes.

From the preceding it necessarily follows that there are gold particles of various size (mass), which for the most part diffract green light, and which when spread through a fluid, endow it with a light absorption whose maximum is in the green; and on the other hand, that there are gold particles of various sizes which diffract chiefly yellow or red light, and also communicate to the fluid a corresponding light absorption. *For this reason, and also because of the facts developed by the study of gold ruby-glasses, we may regard as ill conceived any attempt to calculate from the light absorption the size of the particles in metal hydrosols.* Considerable significance must be attributed, without doubt, to a series of unknown factors (form and shape of the particles, substance of the subdivided metal, and others besides).

That the substance of the subdivided metal is not without influence upon the color of the diffracted light, is quite evident from the fact that in the case of gold we

[1] Siedentopf and Zsigmondy, p. 30.

always find red, green, and yellow particles, with palladium and platinum, mostly white or gray-white (with slight shading); and with silver the most variously colored particles with a brilliant play of colors, all of which will be later referred to (Chapter XIX).

CHAPTER XII

THE COLOR CHANGE OF COLLOIDAL GOLD

If an electrolyte is added to a red colloidal gold solution, the solution changes color from red to blue. This color change indicates an irreversible change of the colloidal gold; if the gold is pure, under no circumstances can it be made retrogressive. If, however, protective colloids are present, the color change of gold may be made reversible. Faraday had already observed that "jelly," when dried out with gold chlorid, etc., became red or blue after drying, and that the blue jelly became red again upon moistening. Preparations exhibiting a similar striking color-play upon moistening or drying, had been obtained by me several years ago by drying bright red colloidal gold solutions with very little gelatin. The thin skin of gold-gelatin remaining, became red when moistened and blue again when dried. This change of color may be repeated as often as desired, and recalls the color change of blue cobalt chlorid upon treatment with water. As Kirchner[1] has shown, silver bromid-gelatin plates, made and developed according to Lippmann's method, in which colloidal silver is the color-producing constituent, show a similar color change upon moistening.

In collaboration with F. Kirchner, there was under-

[1] F. Kirchner, Ber. d. math.-phys. Klasse d. Kgl. Sachs. Ges. d. Wissensch. zu Leipzig, 1902. Further Inaug.-Diss., Leipzig, 1903.

taken an elaborate investigation of gold-gelatin mixtures.[1] The gold solution used for their preparation was the fluid Au_{97} (see Table V, Chapter IX), containing 0.005 per cent of metallic gold. The average mass of the individual particles was 7.10^{-14} mg., corresponding to a diameter of $15\mu\mu$. The number of gold particles per cubic centimeter was about 0.7 milliards. Each fifty cubic centimeters of this gold solution was mixed with varying quantities of gelatin (from 0.5 to 10 parts of gelatin to one part of gold), and the mixtures, after being dialyzed in a closed vessel, were poured out upon glass, etc. Upon drying there remained a blue or dark violet film, which when moistened showed the color change referred to, and when examined by transmitted light with microscope objectives of highest aperture, was resolved into a mass of extremely small, intensely-colored granules, imbedded in an apparently colorless matrix. Each individual granule contained several hundred (larger granules, even several thousand) submicroscopic particles. In them the α-particles (Chapter I) are not inseparably united; they (the β-particles) consist of a mass of gold and gelatin very rich in gold (both apparently equally distributed), imbedded in colorless gelatin. On boiling with water the original subdivision of the gold can be reproduced. Upon drying out, therefore, numerous gold particles have formed a little group, just as do the particles of a pure hydrosol upon the addition of salt. In each case the color changes from red to blue, and in each case the cause of the color change is the same. The original α-gold particles (see Chapter I), which we may consider as resonators,[2] approach each other, and this approach

[1] Kirchner and Zsigmondy, Drude's Ann., 1904, Vol. XV, pp. 573-595.

[2] Metal particles had been previously conceived of as resonators by

influences their time of vibration. The chief cause for the formation of "flocks" in water and groups in gelatin, appears to us to be the attractive forces (cohesion forces) between mutually similar gold particles, which tend to unite them. The great influence of cohesion upon optical constants has been already pointed out by Wernicke.[1] M. Planck[2] advanced a dispersion theory for isotropic dielectrics based upon the assumption that fixed resonators are distributed in the ether, and comes to the conclusion that the crowding together of the resonators has as a result an increase as well as a broadening in the maximum of absorption, which takes place more quickly toward the red than toward the blue. These very changes in the maximum of absorption are clearly evident in Kirchner's silver preparations, as well as our gold-gelatin preparations. The application of Planck's theory to the latter showed quite a complete arrangement between the calculated and empirically determined absorption curves, confirming the correctness of the assumption that the cause of the color change is to be sought for in the change of the distance between the particles. As to the differences between theory and experiment, and for all details, I must refer to the paper cited.[3]

It might be remarked in passing that these experiments may have theoretical importance in regard to many solid colors, ultramarine among others.

Wood, Kirchner, Kossonogow, Ehrenhaft. (Literature in the papers quoted.)

[1] W. Wernicke, Wied. Ann., 1894, Vol. LII, p. 515.

[2] Planck, Drude's Ann., 1900, Vol. I, p. 92. Sitzungber. d. Kgl. Akad. d. Wissensch. zu Berlin, May 1, 1902.

[1] Regarding the optical behavior of colloidal metals, see further Ehrenhaft, Ann. d. Phys., 1903, Vol. II, p. 489. Mention must also be made here of the detailed theoretical investigations as to the origin of the colors of metal hydrosols carried out by G. Mie, Drude's Annalen, 1908, Vol. 25, p. 377, and by Maxwell Garnet, Phil. Trans., 1904, Vol. 203, p. 385, and 1906, Vol. 205, p. 237.

CHAPTER XIII

THE PRECIPITATION AND PROTECTION OF COLLOIDAL GOLD

THE *coagulation* of colloidal gold by the addition of electrolytes is not easy to follow ultramicroscopically. It usually takes place so quickly that there can be seen only the result of the union of the small particles, not the actual process. Sometimes, however, it can be observed.

I shall now describe Experiment No. 2 of Table V, page 132. The light-cone becomes visible; wavy yellow nebulosities are seen; the fog thickens still more, and then appear tiny individual particles having an active Brownian movement. The particles unite and turn about their common center of gravity. After their union, a "molecular motion" begins again, but a slower one than before.

The process does not always proceed as just described; here too a great multiplicity of phenomena appear. If under the microscope the electrolyte solution is allowed to run into the gold solution, there is such a violent whirling that the course of the coagulation cannot be seen; when the fluid comes to rest, the union of the particles has been completed.

If a gold solution with visible particles is very largely diluted, the process of union is hindered, and there are usually seen larger gold-glinting particles, together with smaller green ones which attract each other, but for the most part separate without uniting.

By adding gelatin to the coagulating fluid, one can interrupt the course of the union of the particles at any desired moment. Nos. 18 and 19 of the table are two experiments of this kind. In Experiment 18 the gold particles of Au_{90} have united into smaller flocks than in Experiment 19.

Colloidal Gold and Fuchsin. As I discovered several years ago, colloidal gold and fuchsin (or instead of fuchsin methyl violet, Bismark brown, methylene blue), mutually precipitate each other, sometimes almost quantitatively so that the fluid is decolorized (see Chapter III). By means of alcohol, not water, however, a greater part of the dye-stuff can be removed from the precipitate. Before precipitation commences, the mixture of gold and fuchsin first changes to a dirty violet-red; it then contains only large golden yellow particles, in which sometimes the process of union can be seen.

Protective Action. The protective action against the addition of electrolytes, exerted on colloidal gold solutions by numerous colloids, has in many cases been quantitatively determined by me alone or in collaboration with Fr. N. Schulz [1] (see Chapter III, page 79). This protective action can be explained, as I have already remarked, upon the assumption that a gold particle unites with few or many particles of the protecting colloid, or upon the reverse assumption that one particle of the protecting colloid unites with several gold particles.[2]

Protective action can also be explained by assuming that the "suspended" particles are encased in an oleaginous skin of the other colloid, according to the idea [3]

[1] Schulz and Zsigmondy, Beiträge z. chem. Phys. and Path., Vol. III, p. 137 (1902); Zeitschr. f. analyt. Chem., Vol. XL. p. 697 (1901).

[2] Verh. Naturforscher-Vers., Hamburg, 1901, pp. 168–172.

[3] Or by being surrounded by a skin of easily movable fluid, such as Konowalow assumes to exist in turbid fluids in the critical state.

advanced by Quincke.[1] This view, supported as it is by the analogy of the well-known action of surface energy, can be advantageously applied towards explaining the action exerted by protective colloids upon larger suspended particles.[2]

I must not refrain, however, from pointing out certain considerations which are contrary to it, when the particles to be protected are very small, as in the case of gold solutions of the finest kind.

If we consider the dimensions of the molecule in the light of the kinetic theory, the assumption that the smallest gold particles are homogeneously encased by the relatively large gelatin or albumen molecules (providing the amicrons contained in these hydrosols actually are molecules), is untenable.[3]

There is another objection: some gelatin and some glycogen solutions, and many albumen solutions are found to be permeated with ultramicroscopic particles (see Chapters XIX and XX), whose presence must receive consideration even if perhaps they are not the smallest present in the solution and do not contain the real substance of the dissolved colloid. Particles of this kind as well as the smallest particles of the protective colloid can unite with the colloidal gold; even much larger hydrogel particles can fix the gold, as we will see in discussing the reaction between gold and alumina gel.

In the case of the explanation first advanced, therefore, we must bear in mind the possibility that several

[1] Quincke in Drude's Ann., 1902, Vol. VII, p. 95.

[2] Neisser and Friedemann, Münchner, med. Wochenschr., 1903, No. 11.

[3] Compare the linear dimension of the starch molecule (5 $\mu\mu$) calculated by Lobry de Bruyn, and the graphic representation of the relative sizes of ultramicroscopic particles given further on (Chapter XV, Plate IV).

gold particles can unite with one particle of the protective colloid, as well as that one gold particle can unite with several or many particles of the protective colloid.

Unfortunately the reaction between gold and protective colloid for the most part escapes direct observation in the ultraapparatus, at least so far as concerns the smallest gold particles whose behavior would just be the most interesting, for they are just as invisible as the amicrons of the protective colloid. In some cases the reactions between two colloids can be followed to a certain point ultramicroscopically. Two of these cases will be mentioned here. A detailed discussion of the reactions concerned and of the literature on this subject, I shall reserve until later.

Colloidal Gold and Gelatin. A mixture of Au_{90} (0.0005 per cent Au) and gelatin (0.01 per cent), was placed in the ultraapparatus. The activity of the gold particles had somewhat diminished, everything else being apparently unchanged (as compared with a pure gold solution of the same concentration); in the presence of the gold, the much less luminous gelatin particles could not be recognized. With the fluid Au_{90} the particles continuously formed groups and then flew away from each other; the somewhat large addition of gelatin (about one hundred times as much as was necessary to produce a protective effect), appeared to oppose group formation, without, however, destroying the free mobility of the gold particles. Even subsequent addition of $NaNO_3$ altered the microscopic appearance but little. Larger additions of gelatin produced a further decrease in mobility, but by no means destroyed it.

If, however, there is added to the gold just enough gelatin to produce the protective action, no change at all is seen in the mobility of the gold particles in the

ultraapparatus. This fact is of importance because Lobry de Bruyn[1] has attributed the prevention of many precipitative reactions in the presence of colloids to decreased mobility (which was partially the case in the jellies used by him; see Chapter III, p. 78); and recently Müller[2] has advanced the opinion that the protection of the gold is due to the natural increase in viscosity due to the addition of the colloid, which prevents the "suspended" gold from settling. That this latter view cannot be correct is evident from the fact that the slime of quince kernels, despite its viscosity exhibits no appreciable protective action on gold, while traces of glue (0.0001 per cent), which suffice for this purpose, do not, as we have seen, influence the mobility of the particles, and do not hinder the deposition of suspended gold particles if they are large enough to sink to the bottom in water.

From what has been said it follows that under the conditions in question the gold particles remain isolated; the addition of gelatin does not diminish the number of their little reflecting disks, nor is their brightness increased. The union between the gold and gelatin which must on other grounds be assumed, takes place in such wise that each gold particle is united with one or several gelatin particles (which were present in large excess), whereby the gold is protected against precipitation by electrolytes.

Colloidal Gold and the Hydrogel of Alumina. As I have already shown,[3] freshly precipitated alumina takes the gold from a colloidal gold solution, and forms with it a red colored lake, just as carmine lake is formed by

[1] Ber. d. D. chem. Ges., Vol. XXXV, p. 3079 (1902).
[2] Ibid. Vol. XXXVII, p. 11 (1904).
[3] Verh. d. Ges. D. Naturf., Hamburg, 1901, pp. 172–198.

shaking carmine solution with alumina gel. In order to follow the process of union, levigated alumina gel and colloidal gold were simultaneously introduced into the ultraapparatus; the process is not easy to follow, because it is almost completed before the fluid reaches the observation cell; besides, the dazzling brilliancy of the larger gold-laden hydrogel particles prevents one from seeing the individual grains. Sometimes one may see a bright shining gold particle attach itself to the groups. More often the individual gold submicrons unite with small gel particles which have already taken up gold, to form stationary or moving systems.

Here, too, the union takes place in such a way that several gold particles are taken up by one gel particle. The gold united with the alumina is protected against the addition of salt, just the same as that which is combined with gelatin.

CHAPTER XIV

FILTRATION EXPERIMENTS

In order to obtain some insight into the question so important to bacteriology, as to the size of the filter pores of clay filters and filter cells, I made a number of experiments in the filtration through such media of colloidal gold solutions having particles of known size.

For this purpose three different types of filters were selected.

1. Filter cell, candle-shaped, according to Dr. Maassen.
2. Clay filter, bottle-shaped (ballon filter), according to Pukall.
3. Chamberland filter cell.

As may be supposed from the speed with which water filters through, the first named has the largest pores, while the Chamberland cell has very fine ones.

Without going into details, I may mention the important factors on which such experiments are judged.

All three kinds of filters contain pores large enough to allow the passage of gold particles of about $30\mu\mu$ and less. The pores of a cell are of very different sizes, the Chamberland cell containing, for example, large pores, which allow the gold particles to pass through, and others which retain most of them. The size of the pores is, however, not the sole criterion in filter experiments. It is of especial importance in coarser filters, whether the particles to be filtered are held to the

surface of the cell by adhesion or "adsorption" (A), or not (B).

(*A*) In the first instance the substance to be filtered gathers upon the outside surface (and to a certain extent in the deeper pores), and prevents the other particles from forcing their way through; first, because the pores are made smaller; second, because the particles held fast to the surface of the cell repel the freely moving particles following the course of the current.[1]

(*B*) When adhesion or adsorption do not take place, all colloidally dissolved substances pass freely through the cell, providing the pores are large enough.

This latter case occurs, for instance, when a gold hydrosol with particles 20–30 $\mu\mu$, and containing egg albumen, is filtered through a Pukall cell or a Maassen filter. All the gold particles pass quite smoothly through the cell without appreciable change of concentration. The experiments were made with colloidal gold containing egg albumen. The first of this kind were performed by Prof. Fr. N. Schulz at the Physiological Institute at Jena, and I have repeated the experiment several times with the same result.

If the egg albumen or similar protective colloid is omitted, and the pure gold hydrosol used, then matters proceed as in case *A*, and very many gold particles are attached to the exterior surface of the cell (even in cells with large pores), and at once partially, and by prolonged use, totally prevent the passage of the other gold particles. Bredig first observed this in the Pukall filter. I obtained at first a slightly diluted, but finally a totally colorless filtrate; the outer fluid remained

[1] This action may be due to the well-known negative electric charge of the particles, which apparently also affects the adhering gold particles.

unchanged at first, but when the surface of the cell had accumulated sufficient gold, it became richer in colloidal gold in proportion to the duration of the experiment.[1]

The experiment was made with all three filters, yielding the same result, except that the very fine pored Chamberland filter promptly gave a very diluted filtrate.

In the ultraapparatus the filtrates showed the same properties as the original fluid, but the dilution was considerable, fewer particles being in the filtrate; the concentrated exterior fluid contained, however, numerous larger gold particles in addition to the original ones.

The fact that protected gold particles of 30 $\mu\mu$ and over easily pass through Maassen and Pukall filters, should be of interest to bacteriologists. The Chamberland filter, too, contains, besides the very small pores chiefly present, others which permit the passage of particles of the size mentioned.

In order to avoid misunderstanding I may repeat that this experiment can give no direct measure of the size of the pores, because the size of the gold particles has been calculated on the assumption that they are cubical, whereas we know nothing of their actual shape; nevertheless a gold solution with protective colloid added can be used as a relative measure of the size of the pores of various cells.

Perhaps the above remarks may lead to the production of better filters with uniform pores, for it does not

[1] The course of filtration through Pukall cells observed by me, differs somewhat from that described by Bredig, who obtained, upon filtration of his hydrosols, at first a colorless, then a colored, and finally, colorless filtrate again.

appear impossible to fill up the larger pores with a uniform fine-pored film permeable to fluids, by sucking through coarser subdivisions of gold, platinum, or silver.

PLATE III

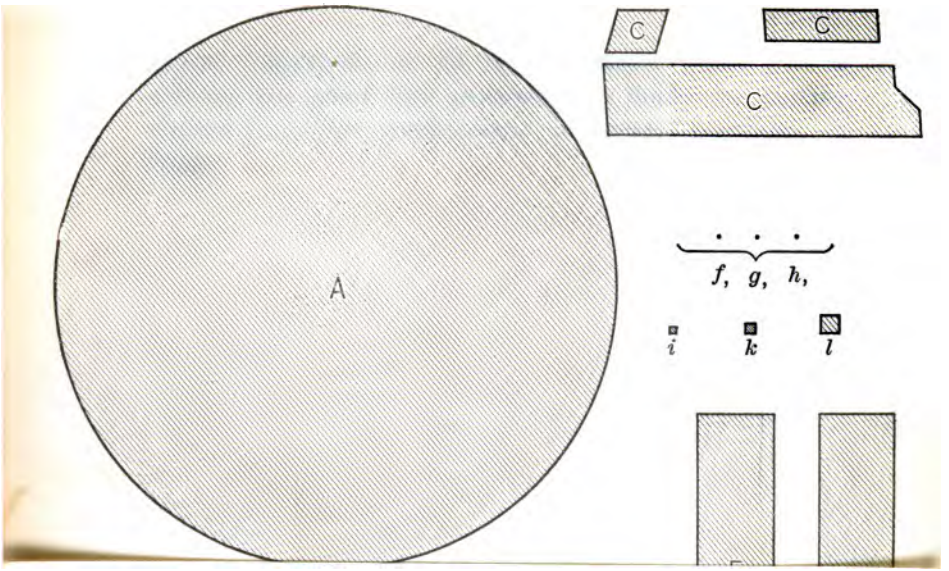
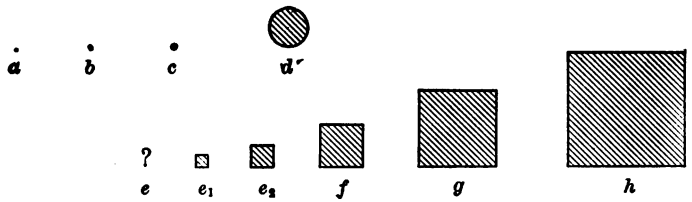


PLATE IV



i

Linear magnification, 1 : 1,000,000

a–d—Hypothetical Molecular Dimensions.

a. Hydrogen molecule—dia. 0.1 $\mu\mu$ (O. E. Meyer).
b. Alcohol molecule—dia. 0.5 $\mu\mu$.
c. Chloroform molecule—dia. 0.8 $\mu\mu$ (Jäger).
d. Molecule of soluble starch—about 5 $\mu\mu$ (Lobry de Bruyn).

e–h—Gold Particles in Colloidal Gold Solutions.

e. Gold particle in AuP_{16} (so small that its size cannot be determined).
e_1. " " " " (about 1.7 $\mu\mu$).[1]
e_2. " " " " (" 3.0 $\mu\mu$).[1]
f. " " " Au_{73a} (" 6 $\mu\mu$).
g. " " " Au_{92} (" 10 $\mu\mu$).
h. " " " Au_{97} (" 15 $\mu\mu$).
i. " " " settled gold suspension *a*.

[1] Zsigmondy, Z. physik. Chem. 1906, Vol. 56, p. 65; Z. f. Elektrochem. 1906, p. 632.

[*To face page* 157.]

CHAPTER XV

THE SIZE OF THE GOLD PARTICLES COMPARED WITH THE SIZE OF OTHER BODIES

FROM the preceding sections it follows that the particles in colloidal gold solutions are much smaller than those of substances that have heretofore been susceptible of direct observation; further, that the size of the amicroscopic gold particles approximates the hypothetical molecular dimensions. In order to show this diagrammatically, I have prepared Plate III, comparing the approximate sizes of several microscopic bodies[1] with those of the gold particles in colloidal solutions—all enlarged 10,000 diameters; in Plate IV the latter are compared with the hypothetical dimensions of the molecule, magnified 1,000,000 times. In Plate IV, instead of the gold particles themselves, whose form is not known, is represented, enlarged a million times, the plane surface of the corresponding cube, which, when filled with metallic gold of twenty specific gravity, would contain the same mass as the gold particles in the fluids Au_{73}, Au_{93}, etc., according to Table V, Chapter IX. Even when enlarged 10,000 diameters, in Plate III, the gold particles *f*, *g*, and *h* in the colloidal solution appear as extremely minute points, while in the same

[1] The figures in the table are meant to express pictorially the relative sizes, and by no means give a true illustration of the bodies in question.

magnification the particles of a blood, starch, or bacteria suspension, assume quite considerable dimensions.[1]

Unfortunately I can as yet give no information as to the size of the particles in albumen and glue solutions, and in the solutions of colloidal oxids and sulphids, for although in many of these individual particles can be made visible, we have as yet no satisfactory information as to their size. As work with the ultraapparatus is now being done in various quarters, it is to be hoped that the desired goal in this direction will soon be reached.

Of great interest are the observations already noted by Raehlmann,[2] that the individual particles in glycogen solutions can be made visible, and that their disappearance upon the addition of diastase can be followed in the ultraapparatus (see also Chapter XX); further, the analogous observation of Römer[3] concerning solutions of true proteins. That the particles made visible in glycogen and protein solutions consist of the essential constituents of the solution in question, appears to be proven beyond reasonable doubt by their action toward specific ferments. That we are dealing here with relatively large particles is evident from their visibility by arc light.

After this significant beginning we may watch with interest the development of this newly-discovered field. It would be a useful and important work for the scientists who make discoveries in this field to determine closely in each case the size of the particles they recognize.

[1] The starch grains of rice are the smallest. Potato starch has granules as large as 100 μ in diameter, and would therefore be one meter in diameter on the scale of Plate III.

[2] Münchner medizin Wochenschr., 1903, No. 48.

[3] Berlin. klin. Wochenschr., 1904, No. 9.

In many colloidal solutions the particles cannot be made visible, which is the case with the colloidal solutions of many metallic oxids. From this it might be concluded that the particles in such solutions are smaller than those in colloidal gold solutions having visible particles. Such a conclusion would be very premature. For the limit of visibility of ultramicroscopic particles has been carefully determined experimentally only for gold; it will vary from substance to substance, and with most bodies be considerably higher than with gold.

The nearer the indices of refraction and dispersion of the subdivided substance and the medium, the less light the particles will diffract, and the larger the particles must be in order to be ultramicroscopically visible. The very appearance of the subdivision clearly shows the difference between noble metals and oxids, etc.

Whereas many fluids appear almost clear,[1] despite the relatively large particles contained in them, gold suspensions with particles of 70–100 $\mu\mu$ show an intense turbidity. Gold and silver subdivided in water disperse light more intensely than do most other substances of the same particle-size. Subdivisions of both noble metals are therefore especially suitable as test objects in ultramicroscopy, because their individual particles can be seen down to extremely small dimensions; but even they, as they become smaller, gradually lose the property of diffracting light—this property almost vanishes as they approach, or when they reach dimensions which the molecular theory ascribes to molecules.

[1] For example, combined suspensions of alumina and iron oxid hydrogel, also of hydrogels of Prussian blue, Congo red, etc.

CHAPTER XVI

SUPERIOR AND INFERIOR LIMITS OF THE SIZE OF THE PARTICLES

Superior Limit. The question as to the superior limit of the size of particles in colloidal solutions should be of some interest. I do not believe that this limit is constant; it will depend upon the specific gravity of the substance subdivided, upon the internal friction of the fluid, and also with many hydrosols upon the electric charge of the particles, and especially upon the manner in which their space is filled with the mass of the subdivided substance. A densely filled particle will tend to sink to the bottom quicker than one which is distended in the filling. Bredig gives as the superior limit of the size of the particles in the metal hydrosols made by him, a linear dimension of 0.14 μ, that is 140 $\mu\mu$.[1]

From Table V, Chapter IX, it appears, however, that gold particles larger than 75 $\mu\mu$ already begin to settle, and up to the present I have not come across any stable hydrosol whose average particle-size was over about 60 $\mu\mu$. On the other hand, in rare instances, I could observe that even bright red gold sols with particles about 30 $\mu\mu$ showed, upon standing perfectly quiet in a room at 4–10° C., a discoloration of the supernatant fluid.

Thus the superior limit for stable gold hydrosols can-

[1] Bredig, Anorganische Fermente, p. 21.

not be determined with accuracy; in any case it is somewhat lower than Bredig has stated. The chance observation above referred to, of the incipient separation of a red gold sol, was of great significance to me, *because it gave me the first indisputable proof that the ultramicroscopic green gold particles are identical with those which gave the fluid its red color;* for the colorless fluid was practically free from ultramicroscopic particles, while the colored layer contained a large number.

The inferior limits of the size of the particles in colloidal gold solutions cannot be experimentally determined with certainty. From Table V (p. 132), Example 1–8, it may be seen that there are a series of transition forms between Au_{73a} having the smallest visible particles, and the gold solution AuP_{16} which, when freshly prepared, is almost homogeneous; and it is evident that the particles of this transition group are *much smaller* than 6 $\mu\mu$. Therefore the size of the gold particles in AuP_{16} surely approach the dimensions of the crystalloid molecule.

Additional questions are also worth discussing: Have we, in gold solutions having the properties of the fluid AuP_{16}, reached the limit of divisibility of the metal, or is there a still more complete solution of it? Colorless, optically clear gold ruby-glass contains such a solution.[1]

[1] This expression needs explanation. Spring had already demonstrated the presence in colorless ruby glass of gas bubbles which destroy its homogeneity. Besides there were frequently found ultramicroscopically large yellow-gold particles in the glass, which had separated out during smelting if the glass was supersaturated. In some varieties, little submicrons can be seen even in the colorless glass. Between these incidental constituents, often scattered in widely separated sections, many kinds of ruby glass show no further inhomogeneity. The space between them appears clear, and, overlooking these incidental

The investigations of Golfier, Besseyre, Knapp, Müller, Ebell, Spring, and others, have made evident, and Spring [1] has also pointed out that in colorless gold ruby-glass we have to do with an optically homogeneous solution of metallic gold. To the objection which might perhaps be raised by those unfamiliar with this field, that we have here to do with the solution of an oxid or a silicate of gold, I may, upon the basis of my entire experience in the glass factory at Zombkowice, reply as follows: Even in the presence of a considerable excess of energetic reducing agents in glass, which certainly had removed all oxygen from the melt and even reduced oxygen present in the gold, upon sudden chilling colorless glasses are always obtained, which when reheated become red. I can therefore confirm the view held by Ebell, Spring, and others, that metallic gold can be dissolved in glass without either coloring it or defracting light. My efforts to obtain a stable, colorless gold solution in water, remain as yet fruitless; in glass, colorless gold solutions are sometimes realized. I do not consider these as colloidal, but essentially as supersaturated, crystalloid solutions of the metal, which view is supported by the observations on the solubility of metals in molten salts, made by R. Lorenz and his pupils.

R. Lorenz [2] first discovered this phenomenon in the

constituents, we may speak of optically clear ruby glass. With other kinds of ruby glass, between the incidental constituents there may be seen an extremely faint whitish light-cone, which quite often is visible only upon the most intense illumination with sunlight (in June when the sun is in high altitude). We have here amicrons, which must be *considerably* smaller than about 4–7 $\mu\mu$; such glasses cannot of course be called optically clear.

[1] W. Spring, Bull. de l'Acad. roy. de Belgique (cl. d. sc.), 1900, No. 12, p. 1017 and 1021 (3d section).

[2] For details see R. Lorenz, Electrolysis of Molten Salts, Part II, Halle a. S., W. Knapp.

electrolysis of molten halogen salts of the heavy metals ($ZnCl_2$, $PbCl_2$, $CdCl_2$, etc.). In these cases there appears about the molten metal which separates out at the cathode, a cloud-effect which spreads through and finally completely fills the molten electrolyte. This phenomenon is easily produced by throwing into a molten salt a piece of the easily fusible metal in question.[1]

The formation of metal fog is dependent upon the temperature, the fog appearing and disappearing in the molten mass as the temperature falls and rises. At higher temperatures it vanishes by solution, and the melt assumes a most characteristic color; upon cooling, on the contrary, it reappears. This solution and reappearance of the fog may be repeated as often as desired by alternately heating and cooling the melting pot.

In collaboration with Helfenstein,[2] R. Lorenz has attempted to find out the relative, so-called solubility of metals in molten salts, and has obtained a series of numerical results.

R. Lorenz[3] also determined, in collaboration with G. Auerbach,[4] that a melt of cadmium chlorid "saturated" with cadmium fog, after cooling and re-solution, leaves metallic cadmium in magnificent little crystals. According to R. Lorenz a far-reaching parallelism can be traced between the formation of metal fogs and the vapor pressure[5] of metals.

The greater the vapor pressure of the metal, the greater should be its crystalloid solubility, and it may well be assumed that at the fusing temperature at which

[1] Zeitschr. f. Elektrochem., Vol. VII, p. 277 (1900).
[2] Zeitschr. f. anorg. Chem., Vol. XXIII, p. 255 (1900).
[3] Zeitschr. f. Elektrochem., Vol. II, p. 318 (1895).
[4] Zeitschr. f. anorg. Chem., Vol. XXVIII, p. 42 (1901).
[5] Zeitschr. f. anorg. Chem., Vol. XXIII, p. 97 (1900).

glass melts (over 1400° C.), a small quantity of gold undergoes crystalloid solution. This solution can be very much overdone, for it is supersaturated [1] even at the working temperature of the glass and sometimes at ordinary temperature after quick chilling.

That colorless ruby glass, too, is probably filled with amicrocsopic gold particles which act as centers of crystallization, will be brought out in the next chapter.

[1] At this temperature the gold separates out in the form of ultra-microscopic particles, often upon slow cooling, almost always upon reheating, but not upon quick cooling.

CHAPTER XVII

AMICROSCOPIC NUCLEI IN COLORLESS RUBY GLASS

If molten colorless gold ruby glass is allowed to cool slowly, according to its quality, it either becomes red [1] upon cooling, or else remains colorless. If quickly chilled to a set, ruby glasses of all grades remain colorless. Colorless ruby glass, as Spring has shown, may be without effect upon light. The normal red color of the ruby glass is almost always brought out by reheating it to the softening point; the color-change thereby produced is technically known as "coloring the ruby glass" (Anlaufen des Rubinglases). After coloring, part of the metallic gold which is homogeneously dissolved in the colorless glass, separates out in the form of ultramicroscopic particles which reflect green light.[2]

1. Gold Particles in Ruby Glass [3]

The gold particles in ruby glass, like those in colloidal solutions, are either submicroscopic or amicroscopic, according to circumstances. Poorly made, spoiled ruby-glass, upon coloring, yields a blue or violet shade instead of red. Below are described the phenomena which may

[1] Glasses very rich in lead, or containing certain impurities, are thereby colored yellow or brown instead of red.

[2] See Siedentopf and Zsigmondy, pp. 19 and 30.

[3] For further information regarding the size, color, and polarization of gold particles in ruby glasses, see Siedentopf and Zsigmondy, loc. cit., pp. 30–38.

be observed in good and in spoiled ruby glass, if both the glasses are heated at only one spot. *With reference to the following observations it must be noted that the glasses under investigation were slowly cooled, and that they were heated up more quickly than they had previously been cooled.*

1. A piece of colorless ruby glass which had been very slowly cooled, was heated at one spot, so that it began to melt at *a* (see Fig. 6), and still remained cold at *d*. At *a* the glass became intensely red, the red color decreasing toward *c*; at *d* the glass remained colorless.

FIG. 6.

2. Spoiled ruby glass becomes blue at *a*, the color decreasing toward *c*; at *b* it is violet, at *b'* bright red, and at *d* colorless.

In the ultraapparatus using homogeneous immersion and brightest sunlight, the following was seen:

Sample I, good ruby glass. At *a* and *b* there were submicroscopic specks of green appearance and very close together; at *b'* a homogeneous green light-cone, becoming weaker as *c* is approached.[1] This light-cone is produced by amicroscopic gold particles. In so far as the individual particles can be traced, their average distance from each other is the same as at *a*, only toward *b'* their brightness considerably diminishes.

[1] With insufficient illumination the light-cone appears homogeneous even at *a*. It is not alone sufficient that the distances between the particles be resolvable; individual particles must also be bright enough to be seen.

Sample II, spoiled ruby glass. The individual particles are much brighter and much further apart than in sample I; they are differently colored, being copper-red at *a*, shading off to yellow, and they are green where the glass is red to transmitted light. Individual particles can be recognized even beyond *c*, and they are, on the average, about the same distance apart, that is, they are just as far apart at *a* as at *b′* and *c*. The brightness of the reflecting disks diminishes from *a* towards *b′*, *c*, and *d*. At *d* faint specks of indefinite color may still be distinguished, but not at all points.[1]

2. On Spontaneous Crystallization

All these phenomena are easily explained, if one recalls the analogy existing between the formation of ruby glass and the devitrification of amorphous substances.

Devitrification of a chilled melt is known to consist of an interior crystallization of the isotropic mass. It is a general rule that in supersaturated solutions crystals can be formed only if centers of crystallization (nuclei), which may either be added or spontaneously formed, are present in the solution. Lowitz, Gay-Lussac, Löwel, Violette, Gernez, and especially Ostwald, deserve credit for a series of excellent researches on this subject.[2]

Among other things Ostwald determined the smallest quantity of crystals necessary to produce the crystallization of supersaturated solutions or supercooled melts,

[1] The above figure is diagrammatic and gives only an approximate idea of the entire process. In Example II the temperature gradient upon warming was greater. Therefore the distance *a d*, as may be imagined, is much smaller than in Example I. Certain imperfections in glasses, such as air bubbles, cloudiness, etc., are not described in order to avoid prolixity.

[2] Ostwald, Lehrb. d. allg. Chem., 2d ed., II, 2, pp. 704–784.

and found it to be 10^{-9} to 10^{-12} gms. in the cases he investigated.

Recently Tammann [1] has made some very interesting contributions to our knowledge of the process of devitrification.

According to Tammann, the spontaneous crystallization of a supercooled melt depends upon two factors: First, its ability to crystallize spontaneously, as measured by the number of centers of crystallization formed

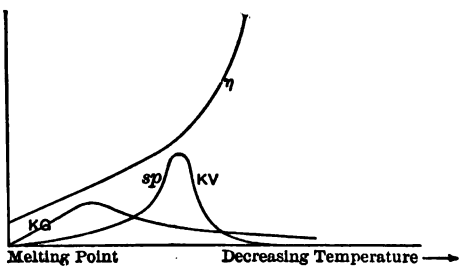


FIG. 7.

in a unit mass of the fluid per unit of time; second, upon the speed of crystallization.

Upon examining organic melts Tammann further found that the number of centers of crystallization per unit of time and weight increased at first as the supercooling increased, but quickly diminished again at temperatures considerably below the melting point. But the number of centers of crystallization formed can be determined only when they have grown to visible size. In cases of excessive supercooling Tammann accomplished this by subsequently raising the temperature high enough to increase the speed of crystallization.

The process for making red ruby pressed glass is

[1] Zeitschr. f. Elektrochem., 1904, Vol. X, p. 532.

quite similar. The glass is first cooled and then heated to redness.

In addition to the power to crystallize spontaneously (*sp KV*) and speed of crystallization (*KG*), Tammann holds that the viscosity (η) of the supercooled melt also influences its behavior. I reproduce from his paper a diagram (Fig. 7), illustrating the dependence of these three properties on the temperature.

The relative position of the three curves is not always the same as here illustrated, for they differ with different substances; the diagram shows, however, that the speed of crystallization and the ability to crystallize spontaneously, increase with diminishing temperature and then decrease again, while the viscosity increases steadily.

3. Spontaneous Crystallization in Ruby Glass

The working temperature of colorless molten gold ruby glass is several hundred degrees lower than the temperature at which it is smelted. If we conceive it, at the working temperature, to be a supersaturated crystalloid solution of metallic gold, and the smallest amicroscopic particles of gold to be centers of crystallization, we can apply Tammann's results to the conditions existing in gold ruby glass. It will at once be seen why ruby glass sometimes remains colorless upon simple cooling, and only becomes red when heated to the softening point. *In this case the optimum temperature for spontaneous crystallization is so low that the glass is very viscous and the speed of crystallization reduced to a minimum.* The nuclei formed by cooling can no longer grow in the almost solidified glass and either remain hidden or lie at the limit of visibility. If by heating the glass acquires a certain mobility, the gold in solution

separates out upon the nuclei present, which by growth become submicrons visible in the ultraapparatus, the glass turning red or becoming darker in color.

That none, or but few nuclei are formed at the higher temperatures at which these centers rapidly increase in size, is evident not only from the fact that the glass examined remained colorless and optically clear[1] *upon slow cooling*, but also from the fact thaat the mean distance between the particles in the reheated glass was just as great at *a* as at *b*[2] and *c*. If new nuclei had been formed during reheating at temperatures favorable to the development of the original nuclei into submicrons, these new nuclei would have developed into submicrons in the strongly heated portion of the glass (at *a*) and there would be more particles per unit volume at *a* than at *b* or *c*. But the number of particles per unit volume was approximately the same in all the variously heated parts of the glass.

If, as in the case in question, the ruby glass is very slowly cooled and then quickly heated again, it is self-evident that most of the gold nuclei must have been already formed during the cooling. Colorless, slowly cooled gold ruby glass contains one part of its gold, therefore, in supersaturated solution, and the rest in the form of nuclei so small that they affect the homogeneity of the glass only slightly or not at all. Upon

[1] The higher temperatures at which the crystals grow quickly are slowly passed by in cooling the molten glass. If nuclei had been formed at these temperatures they would have certainly developed into visible bodies. In the pieces examined this was only partially the case. With other ruby glasses the temperature for spontaneous formation of nuclei is much higher; such glasses color up red upon slow cooling.

[2] In Sample I this was only indistinctly recognizable; in Sample II, distinctly.

subsequent reheating these nuclei serve as centers of growth for separating out the gold dissolved in the glass. The hotter the glass is kept,[1] the more speedily they grow at the expense of the gold in (crystalloid) solution. Therefore (the time of heating being the same) the largest particles are to be found at the places most strongly heated.[2] The gold will continue to separate out until the supersaturation for that particular temperature and glass composition has disapperaed.

Colorimetric tests have shown that in gold ruby glasses under ordinary working conditions, only part of the total gold (about half), separates out in the form of ultramicroscopic particles and serves as a color-producing constituent, the balance remaining in homogeneous solution.

At still higher temperatures the crystalloid solubility of the gold is considerably greater, and by smelting at 1350–1400° C. it is therefore easy to convert red ruby glass into the colorless form, which can again undergo the process of coloring.

Application to Technical Observations (made in actual practice). The value of this view of the coloring of ruby glasses is shown incidentally by the fact that it simply and naturally explains certain heretofore incomprehensible observations made in the course of their manufacture.

Thus it was observed that the rim of a piece of pressed ruby glass remained colorless, while the middle became red. In the press the rim was more quickly cooled than the middle, and by subsequent reheating was heated more quickly and to a higher temperature.

[1] But only to a certain limit of temperature, as will soon be seen.

[2] This heating should not be carried so far that the glass becomes fluid, otherwise the separated gold will redissolve.

Investigation showed that the rim contained a much lesser number but considerably larger green gold particles than the rest of the glass. In the light of the above remarks these facts are easily explained as follows: The rim of the glass had very quickly passed through the optimum temperature for the formation of nuclei, so that only few were formed; subsequent heating to a higher temperature therefore led to a speedy growth of these nuclei into particles of 110–145 $\mu\mu$. The middle section of the same glass had time enough to form a large number of nuclei, which, being less strongly heated, grew more slowly.[1]

In spoiled ruby glass the formation as well as the growth of nuclei is disturbed; fewer nuclei are formed and these grow more slowly than in good ruby glass. In this case I think that instead of simple crystals either crystal-druses or sphero-crystals are formed; if every individual little crystal is conceived to act as a resonator for light waves, such crystals would be able to influence each other differently in the crystal-druse than in simple crystal formation, and thus by displacing the maximum of spectral resonance, produce a change of color in the glass and the diffracting disks. (See Chapter XII [2].)

Difference between Devitrification and Ruby-glass Formation. From what is stated in the present chapter, it is evident that the phenomena which appear during the coloring of ruby glass can be explained by considering the analogy between the process of coloring and that of devitrification, which was closely studied by

[1] The relations are not always as here given; we are considering here only the case where the temperature for the maximum value of *sp KV*. is lower than for the maximum value of *KG*.

[2] In many kinds of ruby glass the color change is due to a conglomeration of the little submicrons into larger ones, in such cases the process is exactly the same as in the coagulation of colloidal gold.

Tammann. *But the coloring of ruby glass should not be confounded with ordinary devitrification.*

The difference between the two is that in the formation of ruby glass several milliards of nuclei exist and grow in a cubic millimeter, and that the hypothetical little crystals, of whose form and structure we know nothing, are so small that their presence changes only the visible appearance and not the working properties of the glass; whereas, in the case of devitrification, relatively few nuclei are present and lead to the formation of quite large crystals, which prevent the usual working up of the glass.

Regarding the size of the smallest gold nuclei hardly anything can at present be stated; for in order to apply the method used for determining their size, an idea must first be formed as to the mass per unit volume of the gold separated out into nuclei. That only a small fraction of the total gold can be present in this form is evident from the fact that most of the gold has the property of depositing upon the centers of growth; but how large this fraction is cannot yet be exactly determined. The next question is, if colorimetry is applicable here; its applicability must first be demonstrated.[1]

Perhaps the intensity of the diffracted light will allow us to form an idea of the size of the particles, providing some relation may be found between their size and their diffracting power.

Preliminarily I might state that the *superior limit* of the mass of the smallest submicroscopic gold particles is from 1.2 to 6.8×10^{-15} mg. (indicating a linear dimension

[1] My recent work on amicroscopic gold nuclei give very promising indications of the applicability of colorimetric methods (Nov. 1, 1908).

of from 4–7 $\mu\mu$),[1] and that they were found in the medium heated portion of a piece of glass which had been heated at one end, as described in the case of good ruby glass on page 166. In the less strongly heated portion of this glass no individual particles could be recognized, but the amicrons present give rise to a light-cone which became weaker as the slightly heated portions of the glass were approached, and finally vanished where the glass was colorless when the opening of the slit was small. Upon opening the slit wide enough and using the brightest sunlight, even here there could be seen a faint but distinct whitish polarized light-cone.

In the sphere of amicrons, therefore, there exist numerous transition forms between the smallest submicrons and the smallest nuclei. If the former consist of several thousand atoms,[2] it is probable that the latter contain only a small number of gold atoms.

Recapitulation. The preceding remarks lead to the assumption that at ordinary temperatures colorless gold ruby glass contains gold in two different forms; most of it is present in supersaturated crystalloid solutions, but part exists as nuclei which at higher temperatures serve as centers of growth, and are so small that their presence influences the homogeneity of the glass slightly or not at all.[3]

[1] Siedentopf and Zsigmondy, loc. cit.

[2] The mass of 1.2 to 6.8×10^{-15} mg. indicates 8 to 42 thousand atoms, if the absolute atomic weight of gold is taken as $= 196 \times 8.2 \times 10^{-22}$. This, however, is the major limit.

[3] In very great thicknesses, which cannot be practically realized, even colorless ruby glass would presumably show some color, just as colorless air appears colored in thick layers. (See p. 7 and Spring, loc. cit., note 1, p. 162).

CHAPTER XVIII

GENERAL REMARKS CONCERNING METAL HYDROSOLS

1. Protective Action of Water

NASCENT gold reduced in water exists in homogeneous subdivision, just as vapor of gold does at first in a very hot tube. Neither in the tube nor in a beaker of water is this subdivision stable at ordinary temperatures; in each case crystallized masses form *if the metal is in sufficient concentration.*

While in the case of gold vapor we have no way of maintaining the original state of subdivision, we do know of methods which, although not always satisfactory, produce approximately this effect if the gold is reduced in fluid media.

One of these methods consists in the very extreme dilution [1] of the mixture employed for reduction.

From *concentrated* solutions of gold chlorid well-formed macroscopic crystals can sometimes be obtained upon the reduction of the metal. Bearing in mind this tendency of gold towards crystallization, it is evident that the more dilute the fluid and the more centers of crystallization formed in the fluid, the smaller the crystals

[1] As brought out in Chapter VIII, the colloidal impurities of water usually tend to prevent the formation of metal solutions, and must therefore be removed as carefully as possible. The above considerations lead to the result that the formation of a metal hydrosol can also take place without the presence of foreign colloids.

will be. If the reduction is effected in very extreme dilution, so that the whole of the chlorid is almost instantaneously transformed into metallic gold, such centers would be simultaneously formed in enormous numbers, and the entire metal content of the fluid consumed either in their formation or in their growth; in the former case there would be obtained an approximately homogeneous fluid with amicroscopic particles; in the latter, a fluid containing amicrons or submicrons, according to the size of the crystals formed.

In fact, every drop of a colloidal gold solution of the latter variety contains milliards of individual particles, indicating the presence of an extremely large number of nuclei during reduction; still much larger must be the number of gold particles and nuclei in the gold solutions which are almost homogeneous. That these particles cannot settle out is evident from the fact that the commencement of sedimentation is observed where the particles are 30 $\mu\mu$; suspensions that settle completely contain particles 80–200 $\mu\mu$ and still larger in size. (See Chapter XVI.)

We can conceive the solutions of colloidal metals to be fluids teeming with such tiny hypothetical crystals.[1] But it would be a grave error to carry the comparison too far and to apply to these extremely fine subdivisions of the substance the results obtained with ordinary suspensions of gold crystals (which do not influence each other). I refer to Chapters I and II, wherein some of the differences are mentioned; I fully believe that

[1] I must here expressly state that I lay no particular stress upon this idea, which would be abandoned if it could be replaced by a better one. It has, however, often been of use to me, and has enabled me to regard things, otherwise difficult of comprehension, from a broad point of view. (See Chapter XVII.)

a world of wonders would be opened up to us if we could observe the actual structure of the particle itself, and its action upon its immediate surroundings.

Graham's remark that in colloidal solutions there resides activity,[1] is especially applicable to colloidal metal solutions. More so than all others do they undergo irreversible changes of condition, changes irreversible in the fullest sense of the word, for all means which, with other colloids, can be successfully used to fluidify the hydrogel formed by coagulation, fail in the case of coagulated pure metal hydrosols. The greatest tendency of these tiny metal particles is to unite into larger complexes, and a variety of trivial causes are sufficient to bring about this union. Upon such union there occurs a much more complete separation from the surrounding medium than with other colloids. This complete separation from the fluid and union of the particles with each other involves a considerable liberation of heat.[2] No actual hydrogel is formed, but a metal-sponge or metallic powder. And even the relatively large particles, of which these latter consist, have not exhausted their tendency toward union. With gold, slight pressure with a polishing iron is sufficient to convert the dried powder into coherent metal, quite in contradistinction to dried hydrogels, which for the most part are friable.

We have characterized the colloidal metal solutions as fluids which, among other things, differ from equally concentrated suspensions of the same metal by their larger energy content.[3]

[1] See Chapter III, p. 34.

[2] See Prange's experiment, p. 15.

[3] The development of heat upon coagulation is explained by the fact that the living force with which the individual particles hurl themselves

It should be remarked that coagulation (in the absence of protective colloids) always begins if the individual particles are brought near enough to each other. It also commences upon the addition of electrolytes whether such addition increases the electropotential difference between the individual particles and the medium (according to Billitzer) or not.

All these facts, together with the impossibility of preparing metal hydrosols from powdered metal in a purely mechanical way, are evidence that with concentrated colloidal metal solutions the process of coagulation must be self-contained, involving the performance of a definite quantity of work, and therefore being associated with a decrease in the free energy.

I consider the attractive forces between the individual particles to be the actuating cause of this process, forces of whose intimate nature we know nothing with certainty, but which are identical with those which oppose the mechanical separation of the united particles (forces of cohesion).

If this idea is correct, the next question is what causes the relative permanence of the dilute metal hydrosols.

It is safe to regard three causes as of importance in producing the relative permanence of such hydrosols: First, the proportionately large distance between the individual particles in dilute solutions, which is unfavorable to their meeting each other. Second, the films of water which immediately surround the particles and are probably held by them with more or less force.[1]

upon each other, becomes heat upon their conglomeration. In the absence of complications, we can calculate therefrom the mechanical work supplied on the average by one particle upon coagulation.

[1] Regarding the pressure of fluids which are absorbed by porous substances, see Lagergren, Zeitschr. f. anorg. Chem., 1900, Vol. XXIII, p. 323. Barus and Schneider also assume aqueous envelopes.

Third, the electric charge of the ultramicrons, which Hardy already regarded as of importance in producing the stability of the irreversible hydrosols.[1]

Finally, the addition of protective colloids materially increases the stability.

The influence of the first cause above referred to is shown by the fact that the change in color of colloidal gold solutions indicative of coagulation and produced by the addition of salt, is retarded if the distances between the particles is increased.[2] On the contrary, if the distances be decreased, coagulation begins spontaneously.

That attractive forces exist between the particles and water is evident from the fact that metals are

[1] Billitzer has already explained this on the sound basis that either anions are given up by the particles or cations are taken up by them. (Bredig had previously expressed a similar view.) If one considers that the formation of colloidal gold proceeds much more smoothly in neutral or faintly alkaline solutions than in slightly acid ones, and reflects that in the former class of solutions the number of hydroxyl ions is vastly greater than in the latter, the idea is easily formed that the charge of the particles is due to hydroxl ions being taken up by adsorption. The assumption that the alkali or another electrolyte, or else some trace of impurity in the water, is absolutely necessary for the formation of a hydrosol, does not seem to me to be of much significance; for the purest water contains in itself all the conditions necessary to give the hydrosol permanence. True protective action by electrolytes is unknown with colloidal metal solutions. On the contrary, the smallest quantities almost always produce coagulation. Furthermore the assumption of a "finest dust" for condensation nuclei appears to me to be superfluous, for if gold is reduced (or vaporized by the electric arc) in a medium in which, as a crystalloid, it is so difficultly soluble as in water, extreme dilution itself will yield all the conditions necessary to the formation of centers of crystallization. But this does not mean that many foreign substances in almost molecular subdivision may not act as nuclei. Perhaps phosphorous proposed by Faraday for reducing gold, or else some of the oxidation products of phosphorous, assume such a function.

[2] See Kirchner and Zsigmondy, Drude's Ann., 1904, Vol. XV, p. 591.

wetted by water and also that pieces of metal take up water from the air, and thus increase in weight. The view that the particles of the surrounding fluid medium which are united with the metallic particles by attractive forces, oppose the union of the latter, is, among other things, supported by an experiment of Barus and Schneider, showing that at critical temperature colloidal silver precipitates from alcohol just as do clay particles from superheated water (Wiedem. Ann., 1893, Vol. XLVIII, p. 335). Thus when fluid and vapor become identical, the protection exercised by the fluid on the metal disappears.

Freezing, the addition of electrolytes, etc., produce a gathering of the particles which cannot be made retrogressive. In short, any circumstance which removes or to a certain degree lessens one or several of the beforementioned influences that give the metal sols their stability, will cause the coagulation of the metal hydrosol, and a complete theory of coagulation cannot therefore allow for only certain of these causes individually, but must take them all collectively into consideration.

Regarding coagulation of hydrosols by electrolytes, it should also be noted that the addition of salt produces not only a gathering but also an electric discharge of the particles, so that according to Hardy the coagulum is isoelectric with the surrounding medium; furthermore, according to Picton and Linder, Spring, Whitney and Ober, Billitzer, and others, there are taken up by the precipitated hydrogel a certain number of such ions of the precipitating salt as have an opposite charge to the particles.

As Quincke has shown,[1] we must also take into con-

[1] Quincke, Drude's Ann., 1902, Vol. VII, p. 95 (paragraph 5). Paragraphs 3 and 4, advanced by Quincke as a basis for explaining the

sideration the eddies produced in the fluid by the addition of electrolytes, for they cause the particles to dash together in a most powerful manner.[1] This influence can be shown to be unimportant by the fact that alcohol and other non-electrolytes produce just as strong eddies and even increase or diminish the difference of electric potential between the particles and the medium, but effect no immediate coagulation of the metal hydrosol.

On the other hand, it must be pointed out that such addition may exercise a protective action, slight or passing though it may be. Thus Blake [2] ascribes to ether a protective action on colloidal gold.

According to what precedes a protective action [3] can be also ascribed to pure fluid water, which prevents the metal particles from forming larger complexes and makes possible the production of colloidal metals. The formation of a colloidal metal solution can be conceived of as a condensation process interrupted in its very incipiency.

It should be noted that electrolytes in general favor the separation of matter subdivided in water, not only bringing about the precipitation of metal hydrosols and of mechanical suspensions, but also diminishing the solubility of non-electrolytes (such as ether, phenyl thiocarbonate,[4] etc.).[5]

turbid solutions of mastic, clay, and oleic acid, are not well applicable to the case in question.

[1] Freundlich has found that solutions of arsenic sulphid are much more indifferent to a very slow addition of barium chlorid than to a sudden addition. Zeitschr. f. phys. Chem., 1903, Vol. XLIV, p. 143.

[2] Blake, Am. Jour. of Sci., 1903, IV (16), p. 435.

[3] No definite idea should be ascribed to the term "protective action," which simply expresses the fact that a union of the ultramicrons is prevented, which, without the presence of water, would doubtless take place at ordinary temperatures.

[4] Rothmund, Zeitschr. f. phys. Chem., 1900, Vol. XXXIII, p. 401; Biltz, Zeitschr. f. phys. Chem., 1903, Vol. XLIII, p. 41.

[5] This action of electrolytes, which extends to crystalloids as well

2. The Finest Subdivisions of Gold

In AuP_{16} we have become acquainted with a gold solution with amicroscopic particles whose dimensions cannot be much larger than those which the kinetic theory of gases ascribes to the molecules of crystalloid solutions; in fact it is still an open question whether the discrete particles in gold solutions of the best kind must be necessarily larger than those assumed to exist in crystalloid solutions of substances having high molecular weight.

That actual discrete particles are to be assumed in the latter follows unequivocally from the research referred to in the Introduction, especially that of Lobry de Bruyn and Wolff,[1] and van Calcar and Lobry de Bruyn.[2]

Barus and Schneider have expressly stated that it is not necessary to assume an allotropic modification of silver in colloidal solutions of this metal, and that it is simpler to hold to the normal molecular weight (which with metals is for the most part the same as the atomic weight).[3]

On page 288 of their article they state:

"The question therefore arises if, under favorable conditions, there may not exist suspensions in whose particles are united 1000, 100, 10, or even still fewer

as to colloids, appears to have its cause not so much in the action of the ions in uniting the particles, but rather in a change in the relations of the medium to the substance subdivided in it, a fact pointed out by Faraday. In the sense expressed by Donnan (Zeitschr. f. phys. Chem., 1901, Vol. XXXVII, p. 741) this may perhaps be expressed by saying that $r < 1$.

[1] Note 1, p. 6.

[2] Note 3, p. 6.

[3] Chapter III, p. 59.

molecules. In extreme instances such mixtures would be difficult to distinguish from a true solution, and in colloidal solutions, we think, we have to do with such extremely fine subdivided sediments."

Apart from the expression "suspensions" and "sediments," which do not appear to be at all appropriate terms for such fine subdivisions,[1] Barus and Schneider have expressed about the same idea that I have formed with regard to gold solutions with amicroscopic particles.

If we imagine a metal solution dissolved in water consisting of an enormous number of metal particles, each of which consists of but few atoms, it is an open question whether, in their totality, these particles could exert osmotic pressure. If we assume that this property is lacking we would have before us an ideal case of colloidal solution. Since it would have no osmotic pressure ("the driving force") [2] it would be incapable of diffusion and be devoid of the property of passing through membranes. Because of the high tendency toward union possessed by their particles, trivial causes would lead to their coagulation; in short, they would have the characteristic properties of typical, irreversible hydrosols.

Such substances would be regarded as heterogeneous in the sense of the phase rule; their particles would grow in a supersaturated solution of the same metal, just like centers of crystallization. (Chapter XVII.) Furthermore, the particles in them would be hardly larger than those in crystalloid solutions; in both, the optical inhomogeneity would almost or entirely vanish. There would therefore be possible *an ideal colloidal solu-*

[1] Instead of the expression "true solution," used by Barus and Schneider, it would be better to say crystalloid solution. See also pp. 1–10.

[2] See Nernst, Theoretische Chem., 3d ed., p. 384.

tion combining with its own essential characteristics the homogeneity of a crystalloid solution. It cannot with certainty be stated whether this ideal limiting case has been realized, but colloidal solutions of the type AuP_{16} closely approach it, with the exception that the dimensions ascribed to molecules actually lie between 0.1 and 1 $\mu\mu$.

The study of the finest subdivisions lying on the border line between crystalloid and colloid solutions, would doubtless be of great interest. It might be anticipated that upon the transition of the crystalloid solution into a colloidal one containing the smallest amicrons, there would be a sudden change in certain properties (such as osmotic pressure, behavior with reagents, etc.), whereas other properties (such as the optical homogeneity) would change only imperceptibly or not at all.

Biltz and Gahl (Chapter XX), have investigated two analogous cases and observed a sudden change in optical homogeneity upon the separation of sulphur and selenium from their crystalloid solution.

The cause of this, according to my experience, is that there had spontaneously formed in the crystalloid solutions of these elements, relatively fewer nuclei than in the finest subdivisions of gold; in the very much supersaturated solution these nuclei had grown with extreme rapidity. With gold solutions it is within our power to permit the simultaneous formation of an extremely large number of nuclei, which soon exhaust the supply of gold and remain extremely small. In such cases the ultraapparatus is incapable of showing the transition from crystalloid to colloid solution, because the optical homogeneity of the fluid is not perceptibly altered by this process.

3. Action of Protective Colloids

We must differentiate two kinds of action exercised by protective colloids: First, protective action upon finished metal hydrosols free from appreciable quantities of foreign colloids; second, protective action in the production of colloidal metals. Regarding the first kind of protective action, the most important facts have been stated in Chapter III and XIII;[1] in addition it might here be mentioned that even protective colloids having the same electric charge as the metal to be protected, exercise a very efficient protection, and that the origin of the protection of the gold can be most simply explained by the assumption that specific attractive forces bring about a union of the ultramicrons of metal and protective colloid, even if both carry like electric charges. That a union actually occurs I have been convinced of several years ago by experiments which cannot be discussed until later.

It has also been stated that in observing certain relations in the "gold figure," we can obtain a relative measure of the protective action upon a certain metal hydrosol.

The second type of protective action, which is closely related to but not identical with the former, comes into play in the production of water or alkali-soluble colloidal metals. They make it possible to obtain very concentrated, water-soluble colloidal metals, which, because of their appreciable content of foreign colloids, may be regarded as analogues of the purple of Cassius, or else as colloid compounds. (Chapter III.)

Here belong the processes for the production of the purple of Cassius, of colloidal metals according to Carey

[1] Pages 81–84 and pp. 150–152.

Lea, Lottermoser and Paal, as well as Möhlau's process for making colloidal indigo.

As to the action of protective colloids in the *formation of metal hydrosols,* only hypotheses can at present be advanced.

It seems to me not improbable that the amicrons of the protective colloid take up by adsorption a part of the dissolved metallic salt, and that the reduced metal then remains united with the amicrons in such fine subdivision that the homogeneity of the fluid is not affected notwithstanding the reduction of the metal. (Some years back I was thus enabled, by reducing gold chlorid in the presence of stannic acid, to obtain purple of Cassius whose solution in ammonia diffracted just as little light as the ammoniacal solution of stannic acid by itself. A faint, polarized light-cone was discernible in both cases).

It can also be assumed that the metallic salt is not adsorbed, but that the reduced metal is taken up by the amicrons of the protective colloid. Finally it appears to be a general property of protective colloids to prevent or interfere with the growth of tiny little crystals. Other less probable assumptions are also possible, but it would take too long to recount them.

Only one thing must be referred to: The protective action is not absolute; the protective colloid is incapable of preventing the incipient condensation of the metal, which would have to be the case in order to obtain stable colorless metal solutions analogous to quickly cooled ruby glass.[1] The protection is quite often so perfect that the metal particles which separate out do

[1] In individual cases temporarily colorless gold solutions may indeed be formed; by indicative measurements the subsequent reduction could be easily determined.

not appreciably increase the inhomogeneity of the solution.

The reactions of metal solutions made in the presence of protective colloids, are chiefly determined by those of the latter; if, however, the metal is present in large excess, its tendency to combine into larger particles comes into evidence, influencing the reaction accordingly.

CHAPTER XIX

ULTRAMICROSCOPIC EXAMINATION OF CERTAIN SOLUTIONS AND SUSPENSIONS

To supplement what has been said in the preceding chapters, there are here given some of my observations on various colloidal solutions and suspensions, and also on solutions of dyestuffs.

Professor Bredig of Heidelberg was kind enough to place at my disposal the following four hydrosols of definite concentration prepared according to his method, for which I herewith tender him my sincere thanks.

Bredig's Gold Hydrosol. The gold hydrosol examined was a fairly clear fluid, purple or violet-red to transmitted light, with a brownish diffuse dispersion. It contained 0.0053 grm. of gold in 100 grms., and $\frac{1}{1000}$ normal NaOH. The fluid contained red, yellow, and green particles; the yellow ones present in the smallest number were usually the brightest, while the red and green ones, present in about equal numbers, exhibited various degrees of brilliancy. All of the particles, however, were considerably brighter than those in my bright red colloidal solutions, for instance Au_{90}, Au_{95}, etc., and despite their active motion had smaller free paths than those in the latter. The amplitude of the translatory motion was generally smaller than 4 μ. Because of the great difference between the particles, their mean size (42 $\mu\mu$), determined by measuring the spaces between them, is naturally of little value. The very brightest

particles could be separated by filtration through very heavy filter paper. By comparing their brightness with that of gold particles in ruby glasses and in gold hydrosols already examined, the size of the particles in Bredig's preparation was placed at 20–80 $\mu\mu$.

Bredig's Colloidal Platinum. A yellow-brown fluid exhibiting slight turbidity to transmitted light (platinum content [1] 0.0034 grm. in 100 cc.). At least four different grades in the sizes of the particles were determined.[2] In contradistinction to the gold particles the platinum particles are not strongly colored, but are all white or rather gray-white, with tinges of yellow or blue. I could recognize no particles with decided red or green color. Although the smaller particles, far outnumbering the larger ones, were much fainter than those in the gold hydrosol previously described, a calculation based upon the distance between them gave as their mean size 44 $\mu\mu$, which indicates that in fine subdivision platinum diffracts less light than gold, the size of the particles being about the same. Feb. 9, 1904.

Bredig's Palladium Hydrosol. (0.0050 grm. Pd in 100 grms.) After long standing (which yielded no sediment), this blackish-brown fluid appeared almost clear. By arc light could be seen single bright white particles with tinges of yellow, blue, etc., and a light-cone due to invisible particles. With the use of sunlight the smaller particles could also be seen; they were not in active motion, and showed no decided color.

Bredig's Colloidal Silver Solution. (0.0038 grm. Ag in 100 grms.) A yellowish-brown fluid showing a gray cloudiness to transmitted light; it can hardly be imagined

[1] The content of this and other colloidal metal solutions were kindly given me by Prof. Dr. Bredig.

[2] By comparing the brightness of the diffraction disks.

what a beautiful color play this unsightly fluid offers upon ultramicroscopic examination. Blue, violet, yellow, green, and red particles of various shades and rare brilliancy of color, move in endless array. One particle approaches another, circles it in a rapid zigzag motion, and is then dashed away again; sometimes one follows another almost in contact but without reaching it. Sometimes several group together and dance like gnats in a sunbeam, especially when, for the fraction of a second, one particle approaches the other. The fluid was examined in various degrees of dilution. Often the influence of one particle on another could be seen even at a distance of 2–4 μ. The linear dimensions of the individual particles was about 50–77 $\mu\mu$.

Silver Hydrosol + NaCl.. The introduction of sodium chlorid solution to the silver sol in the cell immediately produced a whirling together of the particles which made it impossible to observe the process of coagulation. Upon equalization of the differences of concentration by diffusion streams, the considerably larger particles can be seen quietly floating. Sometimes two of these approach each other, but rarely can the process of the union be observed.

Colloidal Silver made According to Carey Lea. Dr. Lottermoser of Dresden was kind enough to send me some colloidal silver made according to the method of Carey Lea, a rather concentrated solution containing 1.276 per cent Ag. Upon dilution this dark brown fluid showed the same splendidly colored picture as Bredig's hydrosol; brought to the same concentration, both fluids would present about the same appearance.[1]

[1] This statement refers to arc light. With sunlight there could be seen in Lottermoser's preparation still *much smaller* particles in very active motion.

A solution of Argentum Credé (solid colloidal silver), obtained more than four years ago from the Heyden Chemical Works, contained somewhat larger and less variegated particles.

Hydrosol of Mercury. The hydrosol of mercury which was kindly placed at my disposal by Dr. Lottermoser,[1] also contained numerous brightly shining, active particles. Unfortunately I neglected to make an immediate thorough examination of this preparation, which is interesting in several respects. As I was about to take up the complete examination after several weeks standing, I was sorry to find that it had coagulated.

Colloidal Ferric Oxid. Two solutions of ferric oxid of different origin were examined; in concentrated solution (1–5 per cent) both showed a very intense polarized bluish light-cone, which became fainter upon further dilution, and in which (besides the diffused light) slow moving individual particles could also be recognized. One of the fluids (*A*) appeared heterogeneous in a concentration of 0.001–0.0005 per cent; the other (*B*) remained apparently homogeneous until the light-cone vanished.

According to this result it seems to me very probable that the solution of ferric oxid, in addition to large individual particles easily made visible, contain chiefly amicrons whose size should be between those of the gold solution AuP_{13}[2] and those of a gold solution of medium subdivision.

As Biltz[3] has found, colloidal ferric oxid and colloidal

[1] A. Lottermoser, "On Colloidal Mercury," Jour. f. pr. Chem., N. F., 1898, Vol. LVII, p. 484.

[2] In which the light cone was much less distinct than in the iron solution of like concentration.

[3] Biltz, Ber. d. chem. Ges., Vol. XXXVII, pp. 1095–1116.

gold mutually precipitate each other. I therefore mixed solution B with AuP_x. Before mixing, individual particles were not to be seen in either, but a short time after mixing there could be seen a large number of bluish-green individual particles, having a brilliancy equal to that of gold particles about 15 μ in diameter, but a much less active motion.

Hydrosol of Silver Iodid. A solution of silver nitrate (0.2 mg. $AgNO_3$ in 100 cc.) was mixed with a very dilute solution of KI. The immediate result was a perfectly clear fluid in which could be seen a blue polarized light-cone. At first no individual particles were visible, but after a long time extremely small particles having active motion could be seen, appearing as blue diffraction-disks. April 7, 1902.

After ten days the particles became distinctly visible by sunlight, their active motion persisting. Calculated from the measurement of the distance between them, the approximate mass of these individual particles was 10^{-14} mg.

Lottermoser [1] has also succeeded in producing concentrated and quite stable solutions of silver iodid. Dr. Lottermoser was kind enough to send me some of his preparation for examination; in this yellowish-white, milky hydrosol, the particles have already grown to considerable size. They are so closely crowded in the concentrated fluid that it is a wonder that so many particles can continue to exist alongside of each other.

The concentrated fluid, Lottermoser states, contained 0.98 grms. silver iodid in 100 cc. In it were seen numberless white particles, rushing past each other as in a surging throng. One extremely important observation should be noted: isolated dust particles and threads,

[1] Lottermoser, Jour. f. pr. Chem., 1903, Vol. LXVIII, p. 341.

sometimes stellated, were surrounded by a ring-shaped (or spherical) space, optically transparent, into which no particles of silver iodid could force their way.

Upon further dilution the color of the individual particles became evident; they were mostly bluish-white, some being yellow-white and some greenish-white. Average size of particles about 60 $\mu\mu$. April 7, 1902.

Iodin Suspension. An alcoholic solution of iodin was poured into water, until a permanent turbidity was produced. Extremely bright shining particles could be seen, some showing slight Brownian motion, others not.

As soon as the particles reached the focus of the light-cone, they were dashed back from it as from a racket, in the direction of the light rays.[1] This phenomenon may perhaps, like the negative photodromy of Quincke,[2] be attributed to the unilateral heating of the suspended iodin. April 2, 1902.

Barium Sulphate Suspension. These were produced with dilute solutions of H_2SO_4 and $BaCl_2$ in varying proportions.

Only larger particles were visible, floating quietly and shining brilliantly.

The crystalloid solubility of $BaSO_4$ appeared to be too great to permit of the preparation of a colloidal solution. Either larger crystals are formed at the very outset, or else perhaps certain crystals grow at the expense of the smaller ones incidentally formed, in analogy with the rule stated by Lord Kelvin,[3] that in vapors the

[1] Upon repeating this experiment two years later I could no longer discover the conditions under which the iodin particles were dashed away.

[2] Quincke, Drude's Ann., 1902, Vol. VII, p. 86.

[3] Lord Kelvin, Proc. Roy. Soc. Edinburgh, 1870, Vol. VII, p. 63.

large drops grow at the expense of the smaller ones.[1] April 4, 1902.

Silver Chlorid Suspension. Lottermoser, in his paper on colloidal silver halids,[2] remarks that the hydrosol of silver chlorid cannot be obtained according to the method described by him for the preparation of silver halids; even when very dilute solutions are used, the resulting fluid is bluish colored to transmitted light, and deposits AgCl. This statement I can entirely confirm. The precipitate yielded by very dilute sodium chlorid with silver nitrate solution, showed a strongly polarized bluish light-cone produced by larger particles having slight Brownian movement. Several experiments made in April, 1902, gave the same result. In one instance the distance between the particles was about 10 μ, the amplitude of the motion of translation about 1 μ. A hydrosol can no more be obtained in this case than in the case of $BaSO_4$, apparently for the same reason. April 7, 1902.

Turbid Solution of Gamboge. The very bright particles exhibit the slow, trembling motion characteristic of the Brownian movement; and to show that the motion of the gold particles is of a quite different nature, it is best to mix the two fluids. While the gamboge particles have a free path of 1–2 μ,[3] that of the gold particles is 10–20 μ and over. April 29, 1902.

Carmine. Levigated commercial carmine exhibited bright red shining particles with but little or no motion.

Solution of Carmine Dye in Ammonia (0.2 per cent carmine). Much smaller particles 6–10 μ apart

[1] According to Ostwald (Lehrbuch. d. allg. Chem., 2d ed., II, p. 757) a solution may be supersaturated as to larger crystals, but hypersaturated as to smaller ones.

[2] Jour. prakt. Chem., N. F., 1903, Vol. LXVIII, p. 343.

[3] In freshly prepared solutions the motion is somewhat more active.

show Brownian movement: $A = 1\text{–}2\ \mu$ (in this and all subsequent cases A denotes the amplitude of the motion in question). The light-cone between them cannot be resolved. The smallest particles are not visible, as I already stated in 1902.[1] April 2, 1902.

Gelatin Solution. A 0.2 per cent gelatin solution two days old appeared heterogeneous. The fluid was entirely filled with small whitish particles at the limit of visibility; along with them were visible much larger hydrogel particles. In a 0.01 per cent gelatin solution the distance between these free moving particles was less than 1 μ; upon further dilution the microscopic picture became indistinct because of the predominance of the diffuse light arising from still smaller particles.[2] March 26, 1902.

Soluble Starch.[3] A 0.01 per cent solution showed by sunlight a distinct but faint diffuse polarized light-cone, together wth few brighter particles. March 14, 1902.

Further remarks regarding soluble starch are to be found in Chapter XXI.

Rice Starch. When levigated in water isolated starch grains, illuminated by the light rays, shine brilliantly, but exhibit no appreciable Brownian movement. April 2, 1902.

[1] Zsigmondy, Zeitschr. f. Elektrochem., 1902, p. 686.

[2] Upon repeating this experiment in the spring of 1904, using a gelatine solution several days old which had been prepared at boiling-point, the light-cone appeared homogeneous, and the individual particles could not be seen. The solution of March, 1902, was probably prepared at medium temperature, and not at boiling-point. As I have already shown (Zeitschr. f. analyt. Chem., 1901, Vol. XL, p. 714), under these conditions there is formed a less perfect colloidal solution of gelatine.

[3] This preparation was kindly given me by Prof. Lintner, of Munich, to whom my best thanks are due.

Starch Paste. In diluted starch paste were to be seen: First, very large and extremely brilliant clumps. Second, numerous smaller particles showing slight Brownian movement. Third, finally upon extreme dilution a distinct light-cone which could be almost entirely blotted out by turning the Nicol. This light-cone became much more distinct after the large suspended particles settled, and upon further dilution assumed a heterogeneous appearance. Iodin colored it blue without facilitating the view of the individual particles. April 2, 1902.

Cigarette Smoke. Gases containing floating particles can be examined in our apparatus just as well as fluids. Cigarette smoke, which can easily be blown into the apparatus through the funnel-tube, exhibits an especially beautiful appearance. By closing the pinch-cock the air enclosed is protected from the motion of the outside currents. The smoke, even when it was very thick, contained particles 10–20 μ apart, which danced about in the elastic medium with an extraordinarily active motion, and as soon as they were struck by the direct sunlight shined most brilliantly. Even their oscillations had an amplitude of 10 μ and over; their motion of translation was considerably more extensive. April 29, 1902.

Fluorescent Dyestuffs. For the sake of completeness I must here mention some experiments made in collaboration with H. Siedentopf, having for their object the examination of solutions of strongly fluorescent dyestuffs in the ultraapparatus.

Fluorescein. A solution of this dyestuff, diluted to 1 : 1,000,000, showed quite an intense light-cone.[1] It was still visible when this solution was diluted a hundred

[1] The depth of the image of the slit was 1–2 μ, its breadth 3–6 μ.

fold, and finally vanished gradually upon further dilution. (As a matter of course a Nicol prism was added as an analyzer, whenever necessary, in order to observe the fluorescent cone alone without interference with the colloids in the water.) Sometimes a kind of cloud formation could be seen, but so indistinct that no conclusion can be drawn from this phenomenon. Several repetitions of the experiment led to the same result, even when objectives made entirely of quartz and fluorspar were used for illumination. April 10, 19, and 23, 1902.

The very strongly fluorescent aescorceïn, which had been kindly placed at our disposal by Prof. O. Liebermann [1] of Berlin, for which we here express to him our sincere thanks, showed under the same conditions a distinct light-cone with a content of $2.5.10^{-7}$ mg. per cubic centimeter. Upon further dilution the light-cone disappeared.

Tetraiodofluorescein behaved in the same manner; several other non-fluorescent dyestuffs were still less visible in solution.

There is, therefore, but little prospect, with the present arrangement of apparatus (especially with the use of arc light), of being able to see the molecules of ordinary dyestuffs which are *dissolved as electrolytes* and *diffuse*, particularly if they exhibit slight or no fluorescence.

On the other hand it is very likely that in the colloidal solution of dyestuffs [2] the individual particles can be seen, if they are large enough; and it is not impossible that the molecules of fluorescent dyestuffs can be made visible, providing they are very large and sufficiently fluorescent.

[1] Liebermann and Wiedermann, Ber. d. D. chem. Ges., 1901, Vol. XXXIV, p. 2611.

[2] Benzopurpurin, for example. (See note, p. 206).

CHAPTER XX

ULTRAMICROSCOPIC INVESTIGATIONS FROM THE PUBLICATIONS OF OTHER SCIENTISTS

Some Investigations of Raehlmann. I have above made mention of Raehlmann's [1] very interesting observation that in the ultraapparatus a large number of submicrons can be seen in a solution of glycogen, also their disappearance under the influence of diastase. Raehlmann was also able to identify albumin particles in the urine of nephritic patients; in this connection he has pointed out that the distance between the individual particles in urine containing originally one per cent of albumin can be measured only after very extreme dilution (1 : 40,000), and that at a dilution of 1 : 500,000 individual particles can still be seen in the solution.

Earlier publications of Raehlmann describe the ultramicroscopic picture of certain dyestuff suspensions and dyestuff solutions and their mixtures.[2] Raehlmann considers the new method of illumination as of especial advantage because it permits particles to be seen in their own color, thereby facilitating the differentiation between particles arising from different dyestuffs. He examined incidentally suspensions of chrome yellow and ultramarine, also the colloidal solutions of Prussian

[1] Raehlmann, loc. cit. (Chap. XV) and Berl. klin. Wochenschr., 1904, No. 8.

[2] Ophthalmolog. Klinik, 1903, No. 16; Ber. d. D. physik. Ges., 1903, Vol. V, pp. 330–339; Physikal. Zeitschr., 1903, Vol. IV, pp. 884–890.

blue, carmine, etc., and described in detail the ultramicroscopic picture of these fluids and their mixtures.

Raehlmann also examined the solutions of the electrolytes, methyl violet and naphthol yellow, and discovered ultramicroscopic particles even in them.

Reference must here be made to the ultramicroscopic investigation of Raehlmann on the constituents of the blood.[1]

Investigations of Much, Römer, and Siebert. Interesting ultramicroscopic investigations were conducted by Much, Römer, and Siebert at von Behring's Institute.[2] In order to obtain a comparative measure for the number of ultramicroscopic particles, these investigators diluted their fluids to such an extent that only 3–4 ultramicroscopic particles were present; the figure expressing the dilution thus obtained was termed the ultra-value. In this manner were examined numerous sera, albumin solutions and wheys.

Just as Raehlmann had been able to see a large number of individual particles in the diluted urine of nephritic patients,[3] these investigators also found individual particles in albuminous urine, their number varying with the severity of the illness. Here, as well as in the following experiments, the ultra-value served as a comparative measure of the number of submicrons. In Table VII which follows, are arranged the results of the examination of the urine of healthy persons and of nephritic patients.

The coincidence between the ultra-value and the results of the boiling test is in every case remarkable,

[1] Deutsche mediz. Wochenschr., 1904, No. 29.

[2] Much, Römer, and Siebert, Ultramicroscopic Investigations. Zeitschr. f. diät. u. physik. Therapie, 1904, Vol. VIII, pp. 19 and 94.

[3] Raehlmann, loc. cit.

and leads to the conclusion that the greater part, if perhaps not all, of the albumin in urine is in the form of ultramicroscopic particles.

TABLE VII

Sample.	Reaction on Boiling.	Ultra-value.
I	0	1:25
II	0	1:60
III	coarsely flocculent ppt.	1:5000
IV	0 (diabetic urine)	1:10 bright light-cone
V	0	1:25
VI	slight turbidity	1:400
VII	coarsely flocculent ppt.	1:10,000
VIII	0 (diabetic urine)	1:30 bright light-cone
IX	opalescence	1:200
X	coarsely flocculent ppt.	1:15,000 {After removal of albumin by boiling with acetic acid} 1:25
XI	"	1: 7,000 {After removal of albumin by boiling with acetic acid} 1:5
XII	"	1:10,000 {After removal of albumin by boiling with acetic acid} 1:35
XIII (Normal urine, exclusive of portion voided in morning)	0	1:50
XIV (Same; 4 o'clock, P.M., after heavy meal)	0	1:20
XV (Same; 11 o'clock, P.M., after light supper)	0	1:20

With this new method of determining albumin care must be taken, because other constituents of the urine, for example the phosphates, which sometimes separate out, may also be present in a similar form.[1]

Much, Römer, and Siebert have, in addition, determined the ultra-value of different sera and colloidal solutions, which are repeated in Table VIII.

Also of interest are the experiments on the digestion of globulin from horse serum by pepsin and hydro-

[1] The authors themselves have referred to the influence of the mucin content.

TABLE VIII

2–4 particles were counted in one field of view of the ultra-apparatus when the fluid was diluted	? Times.	Proportionate Figure.
1. Horse sera:		
Paul serum	100,000	1
Dora serum	80,000	4/5
Ida serum	60,000	3/5
old tetanus serum. Ballon Ia	350,000	3.5
2. Fresh antitoxic horse serum	300,000	3
3. 10 per cent globulin solution from horse serum	20,000	1/5
4. Milk serum	800,000	8
5. 10 per cent solution of Witte's peptone	2,000	1/50
6. 10 per cent atmidalbumose from horse serum	2,000	1/50
7. Marburg nutritive bouillon	250	1/400
8. Urine in slight albuminaria	500	1/200
9. Urine in severe albuminaria	20,000	1/5
10. 10 per cent gelatin solution	4,000	1/25
11. 10 per cent agar solution	10,000	1/10
12. 10 per cent solution of laundry soap	200,000	2
13. 10 per cent mucin solution	300,000	3

chloric acid,[1] and of fat-free milk (ultra-value 750,000), by hydrochloric acid pepsin and pancreatin. A series of remarkable experiments was inaugurated with milk freed from fat, and milk freed from casein by filtration (whey or lactoserum). The wheys of a cow highly immunitized to tuberculosis exhibited bactericidal properties against bacterium coli. These wheys were subjected to electrolysis and an examination made of the anode, cathode, and intermediate wheys. It appeared that the anode wheys showed very powerful bactericidal and agglutinative properties and a high ultra-value, whereas, as may be seen from the following table,[2] the

[1] After incubating for one-half hour the ultra value decreased from 100,000 to 100.

[2] The spore-destroying and agglutinative action referred to is indicated by + + +, when less effective by + +, when very slight by +, and when absent by 0.

cathode wheys were almost free from ultra-particles and entirely free of bactericidal properties.

TABLE IX

	Bactericidal Properties.	Agglutinative Properties.	Ultramicroscopic Examination.
Anode wheys	+++	+++	1:4000
Cathode wheys	0	0	1:50
Intermediate wheys	++	++	1:3400
Non-electrolyzed wheys	+−0	+	1:200

Some Remarks on the Preceding. I cannot here enter into details regarding the work, and return to the method of determining the ultra-value only in view of more recent work in this field. By determination of the ultra-value the authors obtained mutually comparable figures which gave an approximate idea of the relative number of submicrons contained [1] in the fluid. Unfortunately in this work, which was certainly carefully carried out, there are lacking the facts necessary to reach a conclusion as to the absolute number of particles in a unit volume, from which could be obtained an idea of the major limit of the size and the mass of the particles. Such information would certainly have been of general interest and would have made possible comparison with the work of other investigators.

By "field of view" is evidently meant only that part of the field of view directly illuminated, for only in this do the ultramicroscopic particles become visible. The dimensions of the illuminated space can, however, be arbitrarily chosen, and vary according as the light-cone is defined, from front to rear,[2] and according to its breadth and its depth.

[1] Or perhaps formed by dilution.

[2] If the field of view of the eyepiece is taken as a front-to-rear limit,

The value of all future work in this field would be considerably enhanced if the facts as to the number of particles in a given concentration (or else as to the ultra-value) were based upon a certain predetermined illuminated volume of the fluid. This problem would be much simplified for investigators if eye-pieces provided with a suitable Ehrlich diaphragm [1] were commercially procurable; [2] using this, together with definite tube-length and a definite objective, there could, to begin with, be marked out of the light-cone a disk of definite size, having a surface or area of 100 or $200\mu^2$ for instance. The operator has then only to take care that this disk is completely illuminated, and that the light-cone is correctly limited as to depth. By such an arrangement the errors in the determination of volume would be reduced to the errors in the determination of the depth, which are not important factors, because for the most part they are smaller than the errors in the determination of the number of particles.

If the investigators who use the ultraapparatus would take a little care to determine the mean number of particles in a volume of the fluid measured off as carefully as possible, not only would the results of the different experimenters be mutually comparable, but there would also be obtained data for reckoning the

which as a matter of fact is very disadvantageous, the length of the visible portion of the light-cone changes with the nature of the eyepiece used.

[1] Catalogue of C. Zeiss, Mikroskope, 1903, p. 97.

[2] Or a diaphragm with several different large openings so arranged that one can be easily substituted for the other. In fact, H. Siedentopf has recently introduced an eyepiece with checkerboard divisions, which is well adapted for the purpose of counting (Description of the Apparatus for Rendering Visible Ultramicroscopic Particles, Note 3, p. 97). To count submicrons approaching the limit of visibility, I should recommend, however, the eyepiece diaphragm referred to.

approximate size of the particles or their major limit, which information is of greatest importance in the further investigation of colloids.

Furthermore, I consider it dangerous to dilute so far that only 3–4 particles are visible in the whole field, because then the dust particles incidently present in the water used for dilution are also counted in. It is more advantageous to dilute only to such an extent that about 1–6 particles are present in a small, exactly-defined volume (of about 400–1000μ^3). (See remarks on the determination of size.) For dilution, of course, only such fluids must be chosen as produce no precipitative action on the colloidally dissolved substance.

Investigations of Michaelis. From a preliminary communication of Leonor Michaelis,[1] which has recently appeared, we quote the following. Michaelis subdivides dyestuff solutions according to their behavior in the ultraapparatus into:

"(1) **Dyes Totally Resolvable Optically.** Their aqueous solutions even upon extreme dilution, exhibit ultramicroscopically numberless granules. Here belong: First, the aqueous solutions of many heavy molecular sulphoacid dyes, as indulin, violet-black, aniline blue; second, certain pseudo-solutions whose suspension-like nature is probable, even without the ultramicroscope, though it cannot be demonstrated; for example, (*a*) many dyes which, although their aqueous solutions certainly do not belong to this class, exhibit the optical phenomenon of complete granular resolvability, if they are dissolved in aniline water even in a great degree of dilution (fuchsin); (*b*) a dilute solution of scarlet in alcohol, which is then diluted with five to six parts of

[1] Deutsche medizin. Wochenschrift, 1904, No. 42, and Virchows Archiv., 1905, Vol. CLXXIX, pp. 195–208.

water. This procedure precipitates the dye, which of itself is not soluble in water, but it remains in ultramicroscopic suspension; (*c*) a dilute solution of fuchsin in hot, saturated NaCl solution, upon cooling becomes violet or blue to transmitted light, without yielding a precipitate. This solution can be totally resolved optically. After twenty-four hours, the dye generally separates out in flocks.

"(2) **Dyes Partially Resolvable.** These also show granules in the ultramicroscope, but a certain concentration must be reached before a large number is seen. The dye is contained in the solution in two phases, which bear a functional relation to each other; the first being a solution showing nothing in the ultramicroscope, the second being in a form optically resolvable. Here belong the aqueous solutions of fuchsin, methyl violet, and others.

"(3) **Dyes Completely Unresolvable,** but fluorescent. They exhibit an optical inhomogeneity which is macroscopically recoginzed as fluorescence. But with our present methods this inhomogeneity can by no means be resolved into granules even ultramicroscopically. Here belong the aqueous solutions of fluorescein (already examined by Siedentopf and Zsigmondy), eosin, toluidin blue, Nile blue, methylene blue."

The fluorescence observed by Michaelis in methylene blue I can confirm from previous observation.

From the second paper of Michaelis, already cited, I abstract the following remarks:

Bavarian blue also belongs to the completely resolvable dyestuff solutions. Even upon extreme dilution, numberless granules can be recognized in its solution. Although this dye consists of sulpho-acids, and it may be supposed to enter into solution, dissociated into ions

like an electrolyte, nevertheless its aqueous solutions act as hydrosols.

In the second class, in addition to the solutions of fuchsin and methyl violet before referred to, belong the solutions of neutral red, Capri blue, and picric acid. Michaelis is of the opinion that the granules visible in them are not due to an impurity but to an integral constituent of the solution. He bases this opinion on the fact that particles microscopically visible are too profusely and too regularly distributed in the fluid to be regarded as an impurity.[1]

[1] This view is supported by observations made on solutions of glycogen, benzopurpurin, and others. The solutions of benzopurpurin, for instance, show with sunlight sometimes a light-cone resolvable into a large number of bluish-green particles, and at other times a light-cone of the same color, due to amicrons. A freshly prepared solution of this dye-stuff appears turbid because of large particles. In a dilute solution of fuchsin which had stood long enough I could see but few particles, and therefore considered the particles seen by other investigators to be impurities. Solutions of glycogen at the beginning show in the ultra-apparatus more ultramicrons than upon standing. (Raehlmann, Gatin-Gružewska, and Biltz.) J. Lemanissier observed the same thing with hæmoglobin solution. (L'étude des corps ultramicroscopiques, Paris, 1905, Jules Rousset). The solution of hæmoglobin at first shows a large number of submicrons, but after forty-eight hours hardly a particle is left. According to Lemanissier this change is not due to a chemical alteration of the hæmoglobin.

These observations indicate that with many substances the course of solution is a double one, crystalloidal solution occurring simultaneously with a colloidal solution, which for its part may consist either of submicrons or amicrons. From this it is quite evident that determinations of molecular weights with aqueous solutions of fuchsin, methyl violet, etc., made by Krafft (Ber. d. D. chem. Ges., 1889, Vol. XXXII, p. 1612), would lead to a higher molecular weight than determinations with solutions of the same substances in alcohol. With these substances the disappearance of ultramicrons may perhaps be due to a gradual transition from colloidal into crystalloidal solution. With other substance there seems to be a splitting up of submicrons into amicrons, according to the idea of Donnan (Chap. XXI). As may be seen, there are still numerous unsettled questions regarding the

It is known that the acid dyes in general have but slight affinity for cell nuclei. An exception to this are those entirely resolvable optically. These dyes can be used as nucleus-stains, and in addition possess the property of staining evenly. According to Michaelis it is a rule that those dyes which in aqueous solution have the tendency of separating out in granular condition, are the very ones which are adsorbed most readily and in least specific manner by all kinds of organic substrates.

Michaelis further points out that in albumen solutions the granules do not form the whole mass of the albumen, but only a part of it; further, that a different number of particles are obtained according as water or physiological salt solution is used for dilution. The insolubility of globulin in pure water is very well known, as well as the ready partial coagulability of albumen solutions upon mechanical agitation.

That the coagulated particles, before combining into larger ones, first appear as submicrons, is the more evident, because albumen, globulin, etc., are excellent protective colloids,[1] which tend to prevent the formation of visible precipitates. These circumstances suggest care in judging facts ultramicroscopically observed, and, together with the observation, made five years ago, that outside of a few suspended dust particles and a light-cone due to amicrons, crystallized albumen shows nothing, they have led me to exclude albumen solutions from my sphere of work; for until a scientific basis for the method of examination was determined, complications

aqueous solutions of many crystalloids, which can be decided by ultramicroscopy assisted by the application of physico-chemical methods. (Note added while in press).

[1] See Schulz and Zsigmondy, note 3, p. 82.

might easily arise. But this should by no means halt further research. The investigations of Raehlmann, Much, Römer, Siebert, and Michaelis have made evident the fact that submicrons are to be met with more frequently and in larger numbers than had formerly been thought, and they may play an important rôle in life processes which are involved in the mutual reaction between colloidal solutions and hydrogels.

Investigations of W. Biltz. A research carried out by W. Biltz in collaboration with W. Gahl, and reported by Biltz,[1] illustrates how an insight may be obtained into solutions with amicroscopic particles by means of careful ultramicroscopic examination. First are given some precautions regarding the preparation and handling of distilled water to be used for solution and dilution. With both investigators ordinary distilled water yielded unsatisfactory results; for example, 1.6 particles in 0.00004 mm.[3] By combining Spring's precipitation method with careful distillation, they were able, however, to obtain water almost optically clear. By careful filtration through a Pukall filter, there was also obtained water suitable for most uses.

I can certainly confirm the fact that water can be rendered unsuitable for ultramicroscopic uses by stirring it with ground-glass stoppers or filtering it through felt. On the other hand, I have had no unsatisfactory experience with rubber tubes, if they are cleaned by constant washing with water which must now and then be allowed to run through them.[2] For closing flasks containing

[1] Göttinger Nachrichten, math-phys., Section 1904, No. 4. Contributed by W. Biltz.

[2] See p. 112. I have worked much by sunlight with fluids containing almost altogether amicroscopic particles, and was disturbed only a few times by the bad quality of the water. The reason why in my

solutions to be ultramicroscopically examined, Biltz recommends cork stoppers covered with tin foil.

The main subject of the investigation are two reactions: first, the decomposition of thiosulphuric acid; second, the formation of selenium from selenium dioxid and sulphurous acid, both reactions involving the separation of a solid from a solution originally homogeneous. They next undertake to elucidate the phenomena of delay in the action of acids on thiosulphate investigated by Landolt, Foussereau, Hollemann, von Oettingen, and others. As we know, when thiosulphate solutions are acidified, it is some time before the fluid becomes turbid. Foussereau has shown that the decomposition of the acid begins the moment it is formed, and the retardation of the visible reaction is to be attributed to a delay in the sulphur separating out.

It may be assumed that the sulphur is in crystalloidal solution, or that it is colloidally dissolved, in which case the increasing formation of sulphur must gradually change the colloidal solution into a distinct suspension. According to the former view, supported by Ostwald, it is a case of a supersaturation phenomenon, which within a short time is broken up; according to the latter view there is at first formed a microscopic imperceptible colloidal solution, whose particles in time grow large enough to be seen with the naked eye. In the former case the process must be continuous; in the latter, discontinuous.

With the help of the ultramicroscope Biltz and Gahl were able to prove definitely the discontinuity of the process. For several minutes the microscopic picture

investigations especially pure water was needed only in exceptional cases, is because in examining my fluids I generally used a volume fifty to one hundred times smaller than Biltz and Gahl.

remained unchanged, then suddenly appeared an increasing turbidity, with the formation of submicrons.

The ultramicroscopic investigation of the second reaction referred to, illustrates how much difference there is between macroscopic and ultramicroscopic observations. While in the case of the action of sulphurous acid upon selenious acid a turbidity can be macroscopically recognized only after about thirty minutes, upon ultramicroscopic examination, submicrons can be seen separating out in as soon as two minutes and twenty seconds, and this separation considerably increases within the next few seconds. Here too the discontinuity of the process indicates that there is at first formed a supersaturated crystalloid solution of selenium, whose supersaturation is broken down with the formation of submicrons.

An interesting research[1] of Mme. Z. Gatin-Gružewska and W. Biltz deals with the test of the observation of Raehlmann above referred to, that glycogen solutions are filled with ultramicroscopic particles. A particularly pure preparation was made by Z. Gatin-Gružewska in Pflüger's laboratory, and with the observance of all precautions was dissolved in distilled water, which had been purified according to Biltz' method; the solution was examined in the ultraapparatus. By the use of this preparation, Raehlmann's results could also be confirmed, for the 0.07 per cent solution of glycogen showed numerous extremely small white particles having an oscillatory motion. The 0.007 per cent solution also showed a distinct light-cone as well as submicrons. With a concentration of 1:300,000, contrary to Raehlmann's observation, no more than 1–2 particles were to be seen

[1] Archiv. für die ges. Physiologie, 1904, Vol. CV, pp. 115–120.

in the whole field of view; the light-cone was extremely faint but still recognizable.

If, instead of water, alcohol in varying degrees of concentration was used for dilution, the particles increased proportionately with the increasing strength of the alcohol (the final concentration being 0.07 per cent of glycogen).

These experiments prove that in addition to easily recognizable submicrons the aqueous solution of glycogen contains amicrons which, recognizable at first as a homogeneous light-cone, are clumped together into submicrons by the precipitative action of the alcohol. The separation of the dissolved glycogen is not discontinuous, but increases continually with the concentration of the precipitant.

CHAPTER XXI

ON THE FORMATION OF HYDROSOL AND HYDROGEL

1. Sol Formation

It is vain to attempt to convert a practically insoluble substance into a hydrosol by pulverization and levigation. By these means there are always obtained mere suspensions of the substance in question. In order to obtain a hydrosol something else is necessary.

Cohesion very soon sets a fixed limit to mechanical subdivision. It would be of interest to determine this limit for different substances; it would vary from one substance to another, and in the case of friable, soft substances, should not be much lower than a diameter of $\frac{1}{4}$ μ. The difficulty of converting metals into fine powder is very well known; special technical appliances are necessary to do it. But the particles in such powders are still very coarse and cannot be compared with the hypomicrons in metal hydrosols.

There are several ways to obtain hydrosols: (*a*) By the unaided subdivision of a water-soluble colloid in water; (*b*) by peptization, starting with a true hydrogel; (*c*) in some cases by electric atomization of metals (Bredig's process); and finally, (*d*) starting with crystalloids. by the formation, by means of chemical reaction or change of temperature, of a substance within a fluid in which it has practically no crystalloid solubility; this at first leads to the finest subdivisions.

(*a*) *Solution of Reversible Colloids.* A start can be made with the solid form of a reversible hydrosol (solid hydrosol or false hydrogel), which possesses the property of dissolving in water of itself. Donnan[1] has advanced some interesting theoretical considerations regarding this process of subdivision.

Applying the basic principles of capillary theory to the process of colloidal solution, Donnan shows that under certain assumptions the mutual reactions of the forces of cohesion and the forces of molecular attraction can result in an auto-subdivision of the substance, which ceases before molecular dimensions are reached.[2] It should be carefully noted that such a process is possible without any particular solution-tension, that it takes place without the help of electrolytic dissociation and can be explained on the basis of the theory of capillarity, and that it leads to fluids which of course possess no appreciable osmotic pressure.

(*b*) *Peptization and Pectization.* Starting with true hydrogels,[3] which already actually contain pre-formed an extremely fine subdivision, a hydrosol can no more be obtained by simple grinding up with water, than if we had started with an insoluble powder. In order to obtain a colloidal solution from hydrogels it is necessary to add a very minute quantity of a peptisizing

[1] Donnan, Zeitschr. f. phys. Chem., 1901, Vol. XXXVII, p. 735; also 1903, Vol. XLVI, p. 197.

[2] In passing it might be remarked that the process of subdivision can cease when the particles are of medium size, if the bulk of the reversible colloid consists of indivisible submicrons, which are prevented from combining into an inseparable whole by traces of protective colloids, as is the case with Lea's colloidal silver and with colloidal indigo.

[3] A true hydrogel means a jelly which of itself is not soluble in pure water; a false hydrogel or "solid hydrosol" (see Lottermoser) is a water-soluble colloid in solid or semi-solid condition.

substance which need not have any actual chemical action on the hydrosol or its main constituents. The hydrogel then becomes fluid and can be diluted as desired. In this respect many substances show a difference between the true hydrogel[1] and the water-free substance; the latter remain intact and under the same conditions yield no colloidal solution.[2] Stannic acid may be mentioned as an example of this kind. By dilution and careful washing out, a hydrogel, sometimes acid-free, may be obtained from stannous chlorid. As van Bemmelen has shown, the hydrogel of stannic acid is not stannic acid hydrate, as had formerly been assumed, but an adsorption compound of SnO_2 with H_2O. A drop of ammonia can fluidify a large quantity of the gel,[3] but upon being desiccated at ordinary temperature, the stannic acid completely loses the power of being fluidified.

The gel can again be precipitated from the hydrosol of stannic acid by small quantities of acid. Both processes, solution of the stannic acid by alkalis and precipitation by acids, remind one so strongly of chemical reactions, that it seems as if this were a case of an ordinary formation of a salt, and that the hydrosol of stannic acid should be regarded as the solution of an easily soluble salt of the practically insoluble stannic acid. A similar view has recently been adopted by Jordis.[4]

Jordis regards all colloids as amphoteric substances which form salts by acting both as bases and acids,

[1] False hydrogels, such as albumen, dextrin, gum arabic, etc., dissolve in water without the addition of foreign substances.

[2] Therefore in analytical chemistry directions are given in the determination of silicic acid to evaporate to complete dryness.

[3] Zsigmondy, Liebig's Ann., 1898, Vol. CCCI, p. 370.

[4] Jordis, Zeitschr. f. Electrochem., Vol. X, p. 517, and Ber. d. phys.-med. Soc., Erlangen, 1904.

that is, they can act like cations and anions. The same phenomena can be explained from another point of view which can be here only indicated [1]. If the gel of stannic acid be treated with a less concentrated alkali, part of the alkali is by adsorption [2] taken up by the hydrogel; a certain quantity of stannate, K_2SnO_3, may thus be formed. The solution of the gel with the formation of the sol takes place upon dilution with water. Upon dilution, the adsorbed alkali (or the stannate perhaps formed) undergoes electrolytic dissociation precisely as if it were dissolved in water, the dissociation of course increasing with the dilution. In order to understand the process of colloidal solution as well as the behavior upon electrolysis and toward reagents, we must assume in the case of this dissociation that the anion remains adsorbed by the amicrons or submicrons, of which the gel of stannic acid is composed. The adsorbed OH' or SnO_3'' anion gives the stannic acid

[1] I mention these observations only because I have made use of them to advantage for several years past, in order to review the reactions of the purple of Cassius and other colloids, and because their publication may perhaps be of use to others. In fact, quite similar assumptions have been made by Bredig (Anorg. Fermente, loc. cit., 1901, p. 16) and by Swigel Posternak (Ann. Inst. Pasteur, 1901, Vol. XV, pp, 85, 169, 251, and 650), in order to explain peptisation and pectisation.

[1] Or absorption, see van Bemmelen (Chap. III). That adsorption or absorption is still somewhat "mysterious," as is the case with the action of gravity, chemical affinity, and other forces, cannot be doubted; but its presence is indicated by a multitude of phenomena which are neither to be explained by chemical affinity, nor to be referred to other kinds of energy, such as electricity, magnetism, etc. The condensation of gases by charcoal, which was thoroughly investigated by Saussure in 1814 belongs to this class of actions. In Ostwald's Lehrbuch. d. allgem. Chem., 2d ed., I, p. 1084, is to be found a bibliography and critical discussion of this subject. See also E. du Bois-Reymond, Vorlesungen über die Physik des Stoffwechsels.

particles the negative charge which is made evident upon an electric migration test, and effects the separation of the amicrons from each other, as well as their distribution in the fluid. The whole complex (particles of stannic acid with anion attached) acts upon electrolysis just like the complex anion of the alkali salt of a very weak acid; it separates out at the anode, but in contradistinction to true complex ions, cannot pass through the parchment membrane. The reactions of colloidal stannic acid are likewise quite similar to those of the salt of a weak acid. While the behavior of colloidal stannic acid can perhaps be in part explained upon the assumption of the formation of a salt, according to Jordis' idea, such a view cannot hold with many other colloids, the purple of Cassius for instance. This acts just the same as stannic acid, and in order to explain its behavior upon the basis of salt formation, it would be necessary to return to the assumption of Berzelius that the purple is a chemical compound; but this assumption is untenable (see Chapter III, p. 67). Or recourse might be had to the equally erroneous assumption that the metallic gold particles themselves are the anions of a complex salt, or else constituents of such anions, just like platinum in platinochlorids, or iron in potassium ferrocyanid. This assumption contradicts all that we know regarding it: the metallic nature of the individual particles, their incapability of passing through parchment membranes upon electrolysis, and, finally, the fact that very large submicroscopic gold particles consisting of millions of atoms, upon electrolysis, act just the same as the smallest.

In order to give a preliminary sketch as to how these relations may be imagined, a few illustrations are here given.

Designate an ultramicroscopic particle of stannic acid by $\boxed{SnO_2}$ and an ultramicroscopic particle of gold by $\boxed{Au}$. In colloidal solution I believe them to be combined with hydroxyl or with other anions, for example:

$$\begin{array}{c} OH' \\ \boxed{SnO_2} \end{array} \qquad \begin{array}{c} SnO_2'' \\ \boxed{SnO_2} \end{array} \qquad \begin{array}{ccc} & OH' & \\ OH' & \boxed{SnO_2} & OH' \\ & OH' & \end{array}$$

whereby they acquire their electric charge. In the purple of Cassius the gold always remains with the stannic acid, as long as the colloidal condition is maintained. This combination (by "adhesion" [Gay-Lussac], "adsorption" or "affinity of constitution" [1]) can be expressed [2] by

$$\boxed{SnO_2 \mid Au} \qquad \boxed{SnO_2 \mid Au \mid SnO_2}$$

These particles, too, are negatively charged just like those of stannic acid; their charge can be pictorially expressed in like manner, for example:

$$\begin{array}{c} OH' \\ \boxed{Au \mid SnO_2} \\ OH' \end{array}, \text{ etc.}$$

[1] This expression was proposed by W. Biltz. (Ber. d. Deutsch. chem. Ges., Vol. XXXVII, pp. 1112, 1904).

[2] Upon electrolysis the purple separates out at the anode as a red homogenous looking mass, no separation of gold and stannic acid being visible, which would be the case if both constituents were not united with each other (otherwise it may be assumed that the gold and stannic acid would separate the one from the other, according to the intensity of their respective charges and their frictional resistance in the fluid). In fact with an excess of SnO_2 a separation sometimes takes place into red colored purple and colorless stannic acid.

Such signs may be used just the same as chemical formulæ. In contradistinction to the very expressive chemical formulæ, which incidentally express definite proportions by weight, the sign $\boxed{}$ indicates that we are here dealing with a larger complex, with an amicroscopic particle that may perhaps contain as few as several hundred molecules, or with a submicroscopic particle in which may be contained thousands, or even millions, of molecules.[1] But this sign is by no means intended to give any idea of the shape of the amicron or of the way in which its space is filled up.

Neither metastannic acid nor the purple obtained from it dissolve in hydrochloric acid. But solution certainly takes place upon dilution. Just as in the case of peptization with alkalis, we may assume that the gel of metastannic acid absorbs HCl; or else that some stannic chlorid or oxychlorid is formed and thereupon absorbed. Upon dilution, dissociation commences again, and the hydrogen ions (or perhaps the cation of a salt formed from stannic oxid and hydrochloric acid) which are then present in greater concentration, are adsorbed by the amicrons and give them a positive charge.

With the aid of these signs can be expressed in graphic form the most important reactions of stannic acid and the purple of Cassius, as well as those of many other colloid reactions. This method is only indicated here; I must at the same time state, however, that my con-

[1] There is some indication that in this case numerous anions are united by adsorption with one submicroscopic particle, and they then resemble electrode rather than an ion, according to Billitzer's comparison. In opposition to Billitzer, I consider it probable that each individual submicroscopic particle possesses a charge which equals or surpasses that of an ion.

ception is based on Hardy's law of isoelectric state, according to which the stability of irreversible hydrosols depends upon their electric charge,[1] whereas if they lose their potential difference against the medium, they become unstable and coagulate. But Billitzer[2] has shown that certain hydrosols are particularly stable when in isoelectric state, and upon this built up a new conception of coagulation, according to which the ions which produce the coagulation of colloids act as condensation nuclei. Because of the consequences involved in Billitzer's explanation, I will later on take this up specifically, and also those points on which I differ with him.

Whatever particular idea may be formed as to the process of peptization and coagulation, the assumption adopted by Bredig, and also by Billitzer and others, that the particles in the hydrogel are the same as those in the hydrosol and owe their electric charge to an adsorption of ions from the surrounding fluid or to a discharge of ions into it, is certainly capable of more general application to the process in question than the assumption of the formation of chemical compounds, whose existence in some cases cannot be proved, and in other cases must be denied on the basis of the facts.

In this section I must also mention that this very process of pectization and peptization, as well as the precipitation of reversible colloids by NH_4Cl, etc., show such manifold differences in phenomena with each individual colloid, that a complete explanation of these

[1] Other causes which increase stability are mentioned on p. 177. In fact, pure metal hydrosols form a group by themselves, which demands separate consideration. (See Chap. XXI, 2.)

[2] Billitzer, Sitzungsber. der. K. Akad. d. Wiss., Vienna; M. n. Kl., CXI, IIa., Nov. 1902; Zeitschr. f. physik. Chem., 1903, Vol. XLV, p. 107; ibid, 1905, Vol. LI, pp. 129–166.

processes may be safely left to the future. I need but recall the behavior of colloidal silicic acid, which Jordis [1] is studying carefully; also that of globulin and albumen.

(*c*) The conditions under which *metal hydrosols are formed by electric atomization* have been described in detail by Bredig.[2]

(*d*) *Production of colloidal solutions by the formation within a fluid, by chemical means or decrease in temperature, of a substance possessing practically no crystalloid solubility.* We may, in general, assume that most substances are capable of forming crystals. It does not seem improbable that colloids, even if they form jellies, may perhaps consist of submicroscopic or amicroscopic little crystals. Such little crystals, with their water envelopes, must behave quite differently from ordinary microscopic crystals (see further on). The greater the crystalloid solubility of a substance, the larger as a rule will be the crystals separating out from its supersaturated solution.[3] Very insoluble substances like barium sulphate or silver chlorid yield precipitates whose crystal-like nature can hardly be recognized. Nevertheless their solubility is so great that stable colloidal solutions cannot be prepared from these substances. (See Chapter XIX, p. 193.)

In order to obtain stable colloidal solutions by chemical interchange, it is necessary to begin with substances which as crystalloids are practically insoluble. Then

[1] Jordis, loc. cit., and Zeitschr. anorg. Chem., Vol. XLIV, pp. 200–208.

[2] Anorg. Fermente, loc. cit.

[3] Compare Na_2SO_4 with $CuSO_4$ and calcium oxalate. The rule stated serves only for temporary orientation, the size of the crystals depending upon numerous circumstances, important among which are temperature, concentration of the supersaturated solution, degree of supersaturation, etc. But impurities and other influences exercise a considerable effect.

only will the little crystals finally formed remain so small and be able to grow so slightly that there are obtained subdivisions of the degree of homogeneity demanded by colloidal solutions; or else the presence of protective colloids is necessary, which powerfnlly retards the growth of the little crystals, just as it does the union of particles.

It must not pass unnoticed that Nägeli [1] had already advanced the idea that vegetable fibers are formed of micells, molecular complexes optically and structurally anisotropic, that is, of ultramicroscopic structures, whose chief properties are the same as those of tiny anisotropic little crystals. According to Nägeli these micells are approximately uniformly oriented in fibers, thus producing double refraction in them.

H. Ambronn [2] has also frequently pointed out in several papers, that a series of phenomena with colloids (double refraction upon rotation of gelatin, gum solution, etc., or upon stretching gelatin, cherry gum, etc.; also dichroism of dyed fibers and doubly refracting gelatin) may be explained upon the assumption of ultramicroscopic crystals or micells, according to Nägeli's hypothesis. Thus fibers dyed with salts of gold show a wonderful red-greenish blue dichroism, the existence of which, according to H. Ambronn, is most easily explained by the oriented arrangement of the anisotropic little gold crystals. Many phenomena therefore indicate that submicroscopic crystals may have something to do with colloids.[3]

[1] A brief and general statement of Nägeli's views are to be found in Nägeli and Schwendtener, Das Mikroskop, 2d ed., Leipzig, 1877.

[2] H. Ambronn, Ann. der Physik, 1888, Vol. XXXIV, p. 341; ibid, 1889, Vol. XXXVIII, p. 160; Ber. d. D. Botan. Ges., 1889, Vol. VII, pp. 103–114; Ber. d. Kgl. Sachs. Ges. d. Wiss., Dec. 7, 1896.

[3] Dichroism may also be due to differences in the spaces between the

As W. Biltz has also pointed out, the formation of supersaturated crystalloid solutions, even with practically insoluble substances, is more frequent than had been generally presupposed. It is therefore to be expected that upon the formation of a substance having practically no crystalloid solubility, there is at first formed a very strongly supersaturated crystalloid solution. Such solutions, however, are very unstable. In Chapter XVII and XVIII it has already been brought out how amicrons and submicrons can be formed in such supersaturated solutions.[1]

Ostwald has determined the smallest quantity of solid matter which is just able to bring about the crystallization of the supersaturated solution of an easily soluble substance. He found that the limit was about 10^{-6} to 10^{-9} mg.[2] With substances difficulty soluble it should be still less, as brought out in Chapter XVII; and the smallest visible gold submicrons certainly have a mass millions of times smaller than the smallest little crystals extruded (thrown out) by supersaturations of easily soluble substances. But still smaller yet are the amicrons which serve as centers of growth for them.[3] (Chapter XVII.)

particles, that is to an anisotropic lattice-like structure (Ambronn, Ber. d. Kgl. Sachs. Ges. d. Wiss., Vol. XLVIII, p. 622, 1896; F. Braun, Berl. Akad. Ber., 1904, p. 164; Drude's Ann., Vol. XVI; Kirchner and Zsigmondy, Drude's Ann., 1904, Vol. XV, p. 587). As Mr. Ambronn has stated to me that he has recently been able to prepare under certain very simple conditions, very thin needle-shaped microscopic crystals or even little plates united into druses, from gold and silver salts; and these showed just as strong a double refraction with concommitant dichroism as is seen with fibers dyed with gold and silver salts. This rather strongly supports Ambronn's view, above given.

[1] See also Chap. XX, pp. 208–211.

[2] 10^{-9} to 10^{-12} grams, Ostwald, Lehrb. d. allge. Chem., 2d ed., II, 2, p. 784.

[3] The reason for this enormous difference in size is easily compre-

The conditions of colloid formation may be so chosen that only amicroscopic particles are formed (for instance, by extreme dilution of the reacting substances, or by the addition of protective colloids which interfere with growth), and a colloidal solution of great homogeneity may be thus obtained; or they may be so chosen that larger submicroscopic crystals are formed, as, for example, by the use of higher concentrations and by the proper choice of substances having greater speed of crystallization. Under certain circumstances such a case may terminate in a mechanical suspension. By such means can best be studied the influence of the degree of subdivision upon the properties of a substance; careful study along this line promises to bring to light much valuable information, towards which only an incomplete beginning has here been made.

It might here be further stated that increasing the temperature of the reacting mixture (which as a rule increases the crystalloid solubility of slightly soluble substances, besides increasing the speed of crystallization, Chapter XVII) has the effect of causing the formation of

hensible with the aid of Ostwald's classification. Ostwald distinguishes two classes of supersaturated solutions, labile, and metastable. In the former spontaneous crystallization occurs; in the latter it does not, but their supersaturation must be destroyed by a nucleus introduced from without. The limits determined by Ostwald refer to solutions in metastable condition. In the production of precipitates which are difficult to dissolve and of irreversible hydrosols, we are dealing with processes which belong to the labile group.

But the limits given by Ostwald on p. 757, depend upon the degree of supersaturation. The greater the supersaturation in the metastable group, the smaller the crystals needed to resolve it. This very important observation may be applied to the case in point. With increasing supersaturation of the solution of a certain substance, it seems to me that the limit referred to would be quickly carried over into the sphere of small dimensions.

larger particles in the case of irreversible hydrosols.[1] Thus upon the reduction of gold and silver solutions at boiling-point, larger particles are for the most part formed than at ordinary temperatures. It seems to me not improbable that the soluble metalumina and iron metaoxid which Graham considered to be allotropic modifications of colloidal alumina, are to be distinguished from the ordinary hydrosols of these substances chiefly by the size of the ultramicrons contained in them. The formation of the former at higher temperatures and its behavior, and the color and cloudy appearance of iron metaoxid, all point in this direction. Both modifications should yield interesting objects for ultramicroscopic examination.

A considerably different influence of temperature may be observed with soluble starch, which is a reversible colloid. At boiling-point it appears to give a crystalloid solution with very high molecular weight.[2] A three per cent solution prepared at boiling-point shows in the ultra-apparatus even after cooling, a homogeneous polarized light-cone due to amicrons. If this solution is allowed to remain in an unheated room (at about 3–10° C.), it becomes opalescent after a few days, and in three or four weeks changes into a milk-white opaque fluid, which is quite thickly filled with brightly shining particles of 50–100$\mu\mu$.[3]

[1] If the solubility of a substance practically insoluble be increased, then, according to the rule above-mentioned, conditions for the growth of the little crystals are more favorable, and finally larger structures can grow at the expense of the smaller ones.

[2] Because of the size of molecules their general properties cling to colloidal solutions. Lobry de Bruyn figures the linear dimension of the starch molecule to be 5 $\mu\mu$. (Rec. des. Trav. Chem. des Pays-Bas., 1900, Vol. XIX, p. 253).

[3] After half a month the hydrosol changed to a thin jelly; ultrami-

By boiling up, clear solutions can be immediately obtained again. The brightly shining appearance of the particles in the ultraapparatus already indicated that they were not actual hydrogel particles, but were granules of starch heavily compacted.[1] An explanation of the process might perhaps be that at boiling-point an unsaturated crystalloid solution is formed, which becomes much supersaturated at ordinary temperatures;[2] contrary to the usual behavior of crystalloid solutions, the formation of centers of crystallization as well as the growth of little crystals take place with extraordinary slowness. At the same time the amicrons apparently unite to a jelly whose presence is indicated by various circumstances.

The development of submicrons in starch solutions at 3–10° C. recalls vividly the development of gold particles in ruby glass (Chapter XVII), or the process in the production of colloidal sulphur or selenium (Chapter XX). In all these cases a supersaturated crystalloid solution can first be assumed, in which grow the spontaneously formed amicrons and submicrons. Whereas in the last three cases growth takes place speedily at the proper temperature, partially because of the smallness of the crystalloid molecule, its very much more complete diffusion and probably because of a great specific rapidity of growth, that of the starch particles takes place with extreme slowness. It may also be assumed that the starch solution itself contains constituents which oppose growth. With soluble starch, reversion to the original molecular state of subdivision takes place at about

croscopically it could be seen in the diluted fluid that 2–5 brightly shining particles were united together at resolvable distances.

[1] Or else granules made up of smaller but solidly filled submicrons.

[2] Soluble starch swells up in water at ordinary temperatures, but dissolves only to a very small extent.

100° C., and with ruby glass at white heat. It is not improbable that diluted sulphur or selenium solutions can be temporarily changed again into crystalloid solution by heating in a sealed tube.

One remarkable point of difference is that with starch both submicrons and amicrons are considerably larger than those of gold or sulphur, etc., providing that starch molecules have a linear dimension of 5 $\mu\mu$, as Lobry de Bruyn has assumed.

Several cases have been considered in which the growth of the individual particles was explained by assuming that they grow like crystals in a crystalloid solution.

Essentially different conditions may obtain, however, if the enlargement of the particles is consequent upon the union of the tiniest particles, as is the case in coagulation. This process is responsible for many irreversible changes of the condition of colloids. It may, according to the nature of the subdivided substance, lead sometimes to a very intimate, sometimes to a very superficial union, as will be seen later on when we discuss the hydrogels.

How the process of the particles uniting can affect color, has been stated in Chapter XII.

We have described but two kinds of change of condition in hydrosols: the first concerns the growth of small hypothetical little crystals, and results in solid ultramicrons, filled with the matter of the subdivided substance; the other concerns union of the particles of amicrons and submicrons themselves. Both must lead to hydrosols with coarse particles which are different as to quality. Thus the growth of gold particles does not necessarily lead to a color change, whereas the union of particles always does, if the original subdivision was red colored. (See Chapters XII and XVII.)

This does not by any means exhaust the changes in condition of hydrosols; their further discussion at present would not, however, be profitable.

2. A Few Remarks Concerning Gel Formation

We will now consider the final result of the union of particles, as they occur in coagulated masses. From this at once arises the necessity to divide the irreversible hydrosols, which alone are considered in this section, into two varieties, according to the nature and behavior of the coagulum.

Two Classes of Irreversible Hydrosols. To the first class, which may, perhaps, be appropriately called completely irreversible hydrosols, belong colloidal metals which are free from foreign colloids; to the second class belong most colloidal sulphids and many colloidal oxids, which may be called imperfectly irreversible hydrosols.

In Chapter XIX the difference between both classes has already been pointed out. This difference does not as yet appear to be sufficiently appreciated, or it is incorrectly understood, for irreversible hydrosols of the first class have improperly been considered as suspensions, from which they differ not only in degree of subdivision, but also in the nature of their irreversible change of condition.[1] (Chapters I and II.)

[1] There are also mechanical suspensions which undergo irreversible change of condition upon desiccation; but these are not levigated powders of insoluble substances, but levigated powders of hydrogels. The changes of condition of these suspensions, however—and therein lies the essential difference—are not changes of the relation of the levigated hydrogel particles to each other, but changes in the hydrogel itself. They are of exactly the same nature as those which under the same conditions gel-lumps undergo under water.

Difference Between the Two Classes. The most important points of difference between these two classes of irreversible hydrosols are the following:

The irreversible hydrosols of the first class undergo upon coagulation a much more complete separation from the surrounding water; the union of the ultramicrons is much closer; the coagulation is usually accompanied by a change in color. No true jelly is formed, but rather a spongy powder or a metal sponge. All attempts to peptisize the precipitate or change it directly into a hydrosol, are in vain. To obtain a colloidal solution, a salt of the metal must first be formed, and the metal again reduced from this; or recourse must be had to Bredig's method of atomization under water with the electric arc.

The irreversible hydrosols of the second class can easily be prepared a hundred to a thousand times more concentrated than the completely irreversible; if, however, the individual particles are brought near enough to each other (for example, in 1–10 per cent solution), coagulation spontaneously occurs. In dilute solution they are precipitated by traces of electrolytes, just like those of the first group; but here they show a great diversity of behavior; specific influences govern, and the precipitate has all the properties of a hydrogel. When placed upon a filter the precipitate usually appears translucent and jelly-like, just like the hydrogel formed by spontaneous coagulation. The water is so firmly held by it that its complete removal in a desiccator is almost impossible. These precipitates have often been considered to be hydrates, but van Bemmelen has shown that this view is untenable.

While the precipitate is still moist, it is easy, as contrasted with irreversible hydrosols of the first group,

to convert it into a hydrosol again by electrolytes of certain kinds. When air-dried, however, it can as a rule no longer be peptisized. The resemblance and the difference between both classes can at once be seen. With metals there occurs a much closer union of ultramicrons under water, and upon coagulation there is immediately reached the end-point which, with imperperfectly irreversible hydrosols, is reached only upon drying.

A clear idea of the differences between the two classes may be formed by assuming that the water is held to the surface of the amicrons or submicrons of the second class, with much greater force than is the case with metals.[1] In hydrogels of the second class the individual particles are probably separated at first only by an aqueous envelope, but they nevertheless attract each other just the same as do the metal particles, although with proportionately less force because of the greater distance. This attraction, in the absence of any preventative, results in the separation of the hydrosol from the bulk of the water. As soon, however, as the particles receive an electric charge (peptization by electrolytes, Chapter XXI, 1 *b*), they can be separated from each other again because they are not as yet so closely united as the metal particles. Upon further dehydration (which sometimes occurs under water) the hydrogel gradually solidifies; because of the decreasing distance between the particles upon desiccation, the action of the

[1] Quite a rough comparison may serve for an illustration: while a powerful magnet covers itself with a thick coating of iron filings, a weak magnet can hold but few. It requires some force to remove them from the powerful magnet, but they can be easily rubbed off the weaker. The powerful magnet would correspond to amicrons of the second kind, the weak magnet to those of the first kind, but of course only in their behavior with water.

forces of cohesion speedily increases. They not only visibly affect the solidity of the gel, but also militate against the separation of the individual particles by peptization. This does not mean that the process proceeds uniformly throughout the whole mass of the gel; more frequently it goes on at different speeds in different places. If, for example, an attempt is made to peptisize a slightly dried hydrogel, there is sometimes obtained a turbid hydrosol with numerous submicroscopic particles. Van Bemmelen,[1] Bütschli and Quincke have published notable work regarding the structure of hydrogels and their behavior upon desiccation.

Formation of Jellies. According to Bütschli[2] and van Bemmelen,[3] gel formation is to be considered a segregation process, whereby there occurs a separation into two fluids, one of which subsequently solidifies. According to Quincke[4] there exists at the bounding surfaces of what he calls the oleaginous fluid A, a surface tension against the solution B which is richer in water.

Considering the segregation of hydrosols, in accordance with the idea above explained, as conditioned by the mutual attractions of amicrons or submicrons (surrounded by aqueous envelopes), it is at once evident firstly that the precipitate will act like a fluid (even if the individual particles are solid), and secondly, this

[1] See note, Chap. III, p. 73.

[2] O. Butschli, Untersuchungen über mikroskopische Schäume und Protoplasma, Leipzig, 1892; Untersuchungen über Strukturen, Leipzig, 1898; Untersuchungen über die Mikrostructur künstlicher und natürlicher Kieselsäuregallerten, Heidelberg, 1900, p. 343; über der Bau quellbarer Körper, Göttingen, 1896.

[3] van Bemmelen, Z. anorg. Chem., 1898, Vol. XVIII, pp. 14–38.

[4] Quincke, Drude's Ann., 1902, Vol. VII, pp. 57, 631, 701; ebenda, 1903, Vol. IX, pp. 1, 796, 969, ebenda, 1903, Vol. X, pp. 478, 673; ebenda, 1903, Vol. XI, pp. 54 and 449.

fluid will exert an osmotic pressure against the surrounding medium. The fluid properties may be ascribed to the slight friction of the aqueous envelopes against each other, the surface tension to the attraction which the amicrons exercise upon each other through these envelopes. Such attractive forces tend to contract the surface of the precipitate, just as does ordinary surface tension between crystalloid fluids. The fact that hydrogels solidify under water or in the open air, can be considered as consequent upon the co-operation of the attractive forces. As before mentioned, segregation and dehydration do not proceed uniformly throughout the whole mass, but with the formation of a large number of specks which are much coarser than those of the original colloidal solution. Bütschli's microscopic work in particular has been of service in casting light upon this subject. Bütschli examined a large number of hydrogels and almost everywhere found a fine-webbed microstructure, which is usually distinctly visible. By measuring, for example, the diameter d of the little cavities in different silica jellies and by calculating the thickness of their walls m, Bütschli found:

TABLE X

With	d	m[1]
Tabaschir	1.45μ	0.152–0.187μ
van Bemmelen's silica gel	1.00μ	0.27μ
Bütschli's silica gel	1.50μ	0.30μ

In a carefully prepared solution of silica I could find ultramicroscopically, in harmony with the macroscopic

[1] The figures in column marked m are to be considered the major limits of the thickness of the walls. See Bütschli, Unters. über die Mikrostrutur künst. und nat. Kieselsäuregallerten, p. 313.

observation of Picton and Linder, only the slightest suggestion of a light-cone; the silica therefore exists in solution in the form of amicrons, of which size nothing can be accurately stated; it is a substance particularly unsuitable for exhibiting its individual particles. But if we assume that its particles are smaller than 0.005 μ or 0.01μ, an assumption which very probably expresses actual conditions, wc ean then form an idea of variations in the inhomogeneity of colloidal solutions on the one hand and of hydrogels on the other. In any event their amicrons, being invisible upon intense side illumination, are very much smaller than the walls or cavities in the silica gels.

To determine the extent of the effect produced by surface tension upon the formation of the gel skeleton, Quincke conducted a series of interesting researches. "Under the influence of surface tension thin-flowing, oil-like lamellæ form spheres, bubbles, spherical foam-walls, and under some conditions spiral surfaces. Solid thin lamellæ curl up together into a hollow cylinder or hollow sphere. Lamellæ of very sticky, oily fluid lie between them, acting like thin solid lamellæ and curling up into a hollow cylinder or hollow sphere, which then gradually subdivides into spherical bubbles like a fluid tube, or else forms swellings and constrictions." (Drude's Ann., Vol. XI, p. 1035 [8]).

Quincke furthermore could in many cases demonstrate the existence of *invisible* layers of fluid consisting of bubbles and foam walls; he gives eight methods by which this proof can be established. (Drude's Ann., Vol. VII, p. 638.)

According to Quincke, surface tension plays a part in the formation of membranes of precipitates, metal-foliage, and stellate crystals, in modern photogra-

phy, and in the double refraction of jellies and colloids.

This is merely mentioned in passing, just as is the important research of van Bemmelen[1] regarding the physico-chemical behavior of hydrogels, for this book deals chiefly with irreversible colloidal solutions.

In connection with the theory of hydrogels one fact appears to me to be of significance, that from hydrosols of the first class, which of themselves form no true jellies, there can be formed by the addition of small quantities of other colloids, a hydrogel with its characteristic properties (transparency, ability to swell up and [in the case of irreversible hydrosols] to be peptisized). (See "purple of Cassius," etc., Chapter III, also Chapter XII). With a hydrogel, there may therefore be incorporated particles foreign to its nature in such a way that the foreign constituents sometimes constitute the greater part, without materially changing the character of the gel.

In Chapters XVIII and XXI an attempt was made to assemble uniformly several important phenomena concerning irreversible hydrosols, together with the known views published by other investigators, mainly upon the assumption that the ultramicrons in hydrosols consist of the same substance as those in the hydrogels obtained from them.[2] This assumption is by no means new, for Graham, van Bemmelen, Hardy, Bredig, Billitzer, and others assume essentially the same thing. And it

[1] Loc. cit.

[2] The fact supported by Jordis in particular, that irreversible hydrosols have not as a whole the same chemical constitution as the hydrogels obtained from them, is not affected by these statements, but only explained from another point of view. I also agree with Jordis that chemical reactions in cases where they are to be expected must by all means be allowed for.

is also supported by the fact that such submicrons as are concerned in gel formation, as, for example, gold in the purple of Cassius, do not change their properties if they are changed into a hydrogel and then back again into a hydrosol. In the course of time other examples will doubtless be found.

The second assumption made necessary to explain the peptization and pectization of irreversible colloids, namely, that the ultramicrons of colloids can, without being chemically bound, unite with ions which give them an electric charge, naturally follows from the application of the view supported by Nernst in particular—that ions are an independent kind of molecules—to the results of Hardy's investigations. This is by no means a new proposition, for Bredig has already referred the electric charge of colloid particles to the differences of the specific particle coefficients of the ions present; and Billitzer has directly maintained and established by experiments that the electric charge of the individual particles is due to the acquisition or loss of ions.

The third assumption necessary to explain plainly and satisfactorily the course of colloidal solution, the coagulation of metals, the existence of surface tension at the boundary between gel and surrounding fluid, and especially numerous colloid reactions, viz., the assumption of attractive forces between the ultramicrons themselves and between them and the molecules of the surrounding medium, is nothing new either, for the capillary theory of La Place assumes molecular attractive forces between similar and dissimilar substances and thus is able to explain the great variety of capillary phenomena. Similar attractive forces were assumed in colloids even by Gay-Lussac, by Graham (to explain pectization), by Nägeli, and by Barus and Schneider. Donnan has pointed out

the applicability of the fundamental ideas of the capillary theory to what happens during colloidal solution, and paved the way to show that a great number of phenomena can be explained by a few special assumptions regarding the forces in question, without the addition of any new hypotheses. That these forces will vary from case to case, can be seen from the fact that the cohesion of different substances varies greatly in value (van der Waals, Die Kontinuität des gasförmigen und flüssigen Zustandes, 2d Edition, Vol. I, p. 175), and that the surface tension at the boundary between two media is dependent upon it.

From the assumption made by Donnan, of attractive forces between colloid and surrounding medium, to that of attractive forces between colloid particles of different kinds (which in addition to electric charge are connected with colloid reactions), is only a short step. W. Biltz also arrived at a similar conclusion and expressed it in the same way by proposing the term "affinity of condition" (Zustandsaffinität) for the basic causes of absorption processes.

The above explanation is of course not intended as a theory of colloids, for the study of colloids will become a great and extensive science, in the development of which many must assist; it is only when the numerous facts, developed from basic physico-chemical experimental research, have been systematically arranged, that the theory of colloids will be raised from the stage of a generalization of special instances to the rank of an exact science.

RECAPITULATION

THE starting point of this book is a fundamental question of colloidal chemistry, viz., the question whether or not the polarized dispersion of light recognizable in hydrosols by the Tyndall test, is one of the essential properties of hydrosols.

By means of the method developed by Siedentopf and myself, of rendering visible ultramicroscopic particles, this question could in some cases be decided. In the case of the hydrosols examined, the diffuse dispersion of light has proved to be an essential characteristic; it is caused by the same material particles which give to those fluids their otherwise remarkable properties.

The newly developed method for making visible and measuring ultramicroscopic particles, made it possible to obtain a closer insight into the processes and relations in colloidal solutions, hitherto inaccessible to direct observation.

Thus by a series of experiments, the size of the particles in colloidal metal solutions was determined. It was shown that in coarser hydrosols the largest particles have a mass corresponding to a linear dimension of about 60–80 $\mu\mu$ (Chapters IX and XIX), but that carefully prepared solutions show an inhomogeneity which is scarcely discernible and hardly to be distinguished from that of many crystalloid solutions; further, that numerous intermediaries exist between these extreme cases (Chapter IX).

It was shown that the smaller metal particles in hydro-

sols possess an extremely active oscillatory and translatory motion, which in many respects differs from the typical Brownian movement (Chapter X).

The statement made in conjunction with H. Siedentopf, that in the case of metal subdivisions (in ruby glasses) there is no connection recognizable between the size of the particles and their color, was confirmed by the examination of colloidal gold solutions (Chapter XI).

In collaboration with F. Kirchner a closer insight could be had into the course of events responsible for the color changes of metal hydrosols (Chapter XII).

To obtain a preliminary insight into the question so important to bacteriologists, as to the relative size of the pores in the clay and other filters used, some experiments were conducted toward this end (Chapter XIV).

My own experiments and especially the experiments of other investigators (Chapter XX) have shown that the individual particles in many reversible colloids and dyestuff solutions are also capable of direct observation. The possibility of thus forming an idea as to the size of these particles, renders it desirable to have in mind the size of the particles when classifying hydrosols. An attempt in this direction is made in Chapter II. In Chapter XV the sizes of the particles in some hydrosols, experimentally determined, are compared with those in ordinary suspensions.

Since this work makes frequent reference to earlier publications concerning irreversible hydrosols, it seemed desirable to give a brief resumé of the papers on this subject in an historical section, especially as abstracts of them do not always give the authors' views with sufficient accuracy. It seemed desirable to make readily accessible to everyone interested therein the contents of the basic work of Graham on colloids. In the historical portion

his publications on this subject are reviewed at length and in part quoted verbatim.

While actively engaged with the ultramicroscopic examination of fluids, the author learned many facts of general interest, and certain precautions which should be observed; these are mentioned in Chapter VII.

Numerous observations made upon ruby glass have been most simply explained by applying the results of Tammann's work upon spontaneous crystallization of supercooled melts, to what happens in the formation of ruby glass. This made it probable that the formation of red ruby glass is due to the growth of amicroscopic crystals in a crystalloid solution of metallic gold.

It seemed desirable to apply the preliminary insight thus obtained into actions only partially susceptible of direct observation, to what occurs during the formation of hydrosols and hydrogels, and to test upon what premises the assumption of ultramicroscopic crystals could be reconciled with the facts observed in connection with colloids. These and some other questions concerning the theory of colloids, are briefly discussed in Chapters XVIII and XXI.

The numerous methods of chemistry, of physical chemistry, and of physics, to which has recently been added ultramicroscopy, will in proper combination make it possible to settle certain questions the answers to which are of importance for the further development of the study of colloids. Even if the last-named method cannot fulfil the exaggerated hopes sometimes based upon it, present results have shown it is an important supplement to other methods, and permits an insight into relations which, until now, were not accessible either to direct microscopic observation, or to ordinary, physicochemical methods.

EXPLANATION OF THE COLORED PLATES

The gold solutions are arranged in order of the increasing size of their particles; at *A* (Plate I) is illustrated their appearance in incident light, at *C* (Plate II), their appearance in transmitted light. *B* (Plate I) shows the corresponding ultramicroscopic pictures, *D* (Plate II) the macroscopic appearance of the light-cones. The numbers of the fluids are marked upon the cork stoppers.

In Plate I, under the bottles are given the linear dimensions of the gold particles, as determined according to the method described and conditions given in Drude's Annalen, Vol. X, pp. 16–30. For estimating approximately the size of the particles in amicroscopic hydrosols, there was used a new method, the principle of which is given in the Zeitschrift für physikalische Chemie, Vol. LVI, p. 68, and in the Zeitschrift für Elektrochemie, 1906, p. 631.

The solutions shown each contain the same quantity of gold, i.e., 0.005%. The ultramicroscopic images as well as the macroscopic light-cones were observed and drawn after diluting each fluid ten times. (In examining the ultramicrons of fluids, 0 to 4, the isolated, brighter, yellow particles should be disregarded. Because of dust particles they form an incidental impurity of the fluid, difficult to avoid; it must also be stated that it is impossible to reproduce, true to nature, the brilliant light emitted by the gold particles in Fluid *5a'* and especially in Fluid 6. The gradations of brilliancy are naturally considerably greater than appears from the illustrations. The red colors of the fluids 0 to 4 are more vivid than in the illustration. The light-cone of Fluid 1 is distinctly green; that of Fluid 0 has no recognizable color.)

At the right is a suspension that settles (No. 6), with particles of 100–150 $\mu\mu$, a turbid, faintly colored fluid whose ultramicroscopic image consists of few very intensely luminous submicrons.

With decreasing size of the particles the brilliancy of the submicrons considerably decreases; from about 50 $\mu\mu$ and under, the brilliancy of the light-cone also decreases.

The almost-clear fluid marked No. 3, contains gold particles 20–25 $\mu\mu$ in diameter, all quite visible and mostly green. As is the case with

the subsequent numbers, 0 and 1, it no longer settles, and furthermore exhibits the properties of a colloidal solution, especially the irreversible changes of condition characteristic of such solutions.

With further subdivision, the brilliancy of the ultramicrons speedily diminishes, and we soon reach the amicroscopic field, where can be seen the light-cone but no individual particles. The fluid marked *O* (with particles of about 2–3 $\mu\mu$, not 0.2–3 as erroneously given on the plate), is an example of this class. It appears completely clear both in incident and in transmitted light, and its Faraday-Tyndall light-cone (see *D*, Plate II) is fainter than those of the other fluids.

Sometimes there can be obtained still finer subdivisions, that show in the ultraapparatus only individual dust particles, between which the fluid appears optically clear. Fluids of this kind contain particles still smaller than those previously described; they resemble the latter completely in superficial appearance and behavior, and their existence is a proof that gold itself can be subdivided until it is *optically* homogeneous.

COLORED PLATE I

Subdivisions of Gold in order of increasing size of particles (R. Zsigmondy).

A. Appearance in incident daylight. B. Ultramicroscopic images of the subdivisions.

COLORED PLATE II

Subdivisions of Gold in order of increasing size of particles (R. Zsigmondy).

C. Appearance in transmitted light.

D. Macroscopic appearance of the corresponding Faraday-Tyndall light-cone.

INDEX

PAGE

Absorption....73, 215
Absorption and adsorption.... 73
Absorption compounds....68, 69
Adsorption....73, 215
Æscorcein, examination of.... 197
Albumen—Grahams' work on.... 44
Albumen, protective action of....81, 82, 87
Albumoses, action of, on colloidal gold....82, 83
Alcogels.... 50
Alumina, soluble.... 38
Amicrons, definition of.... 110
Aniline dyes, ultramicroscopic examination of.... 204
Antitoxins and toxins, mutual reactions of.... 73
Antitoxins, gold figures of.... 84
Argentous oxid.... 70
Argentum Credé.... 191
Aurous sulphite.... 70

Barium sulphate suspension.... 193
Benzopurpurin.... 206
Bredig's hydrosols.... 188
Brownian motion.... 137

Cæsium subchlorid.... 69
Capillary theory as applied to colloidal solution.... 213
Caramel.... 43
Carey Lea's colloidal silver.... 190
Carmine.... 194
Casein, protective action of....81, 87
Chamberland filter, experiments with.... 153
Chemical compounds, simulation of, by colloidal mixtures.... 67
Chromium oxid, soluble.... 41
Cigarette-smoke, ultramicroscopic examination of.... 196

Classification of colloids: PAGE
Graham's. 22
Hardy's. 19, 23
Müller's. 19
Zsigmondy's. 25
Cohesion, influence of, on optical constants. 146
Colloid compounds. 68, 69, 74
graphic representation of. 217
simulation of chemical compounds of. 70, 74
Colloid mixtures. 68
Colloidal antimony sulphid. 57
Colloidal arsenic sulphid. 57–62
Colloidal condition. 44
Colloidal copper sulphid. 57
Colloidal ferric oxid. 191
Colloidal gold. 74
Colloidal gold and alumina. 151
Colloidal gold and gelatin. 150
Colloidal gold, coagulation of. 147
Colloidal gold, coagulation of by electrolytes. 78
Colloidal gold, color changes of. 144
Colloidal gold, color of particles of. 141
Colloidal gold, color-producing particles in. 161
Colloidal gold (Bredig's) examination of. 188
Colloidal gold, finest subdivisions of. 182
Colloidal gold, limits of size of particles in. 160, 173
Colloidal gold, motion of particles of. 134
Colloidal gold, preparation of. 124
Colloidal gold, relative size of particles in. 157
Colloidal gold, ultramicroscopic examination of. 129
Colloidal mercury. 191
Colloidal metals. 63
Colloidal metastannic acid. 54
Colloidal mixtures. 67, 68
Colloidal molybdic acid. 56
Colloidal palladium. 189
Colloidal platinum. 189
Colloidal selenium. 210
Colloidal silicic acid. 35–47
Colloidal silver. 59
Colloidal silver, examination of. 189, 190
Colloidal silver, heat developed by the coagulation of. 15
Colloidal silver iodid. 192
Colloidal solutions, characteristics of. 11

PAGE
Colloidal solutions, definition of. 23
Colloidal solutions, distinguished from crystalloidal solutions. 11
Colloidal solutions, distinguished from suspensions. 12
Colloidal solutions, nature of. 89
Colloidal solutions, ultramicroscopic examination of. 113
Colloidal stannic acid. 54
Colloidal sulphids. 57
Colloidal titanic acid. 54
Colloidal tungstic acid. 55
Colloidal ultramarine. 58
Colloids, Jordis' views on. 126, 214
Colloids, preparation of by dialysis (Graham). 34
Colloids, protective action of. 185
Color lakes, colloidal nature of. 74
Crystallization, prevention of, by protective colloids 186

Devitrification. 167
Dextrin, protective action of. 81, 87
Diastase, appearance of action of, on glycogen. 198
Dichroism in fibers. 221
Distilled water, ultramicroscopic examination of. 112
Dyeing, colloidal theory of. 74
Dyes, examination of. 198, 204

Energy of colloidal solutions. 90, 91
Faraday-Tyndall method. 3
Faraday-Tyndall test, sensitiveness of. 96
Faraday's researches on colloidal gold. 75
Ferric arsenite. 73
Filtration experiments. 153
Fluorescein, examination of. 196
Fluorescent dyes, examination of. 196

Gamboge solution. 194
Gelatin, relative protective action of. 80, 81
Gelatin solution, ultramicroscopic examination of. 195
Gels, formation of. 230
Globulin, digestion of. 200
Globulin, protective action of. 82
Glue, protective action of. 81, 87
Glycogen, action of diastase on. 158
Glycogen, disappearance of particles in. 206

PAGE
Glycogen, examination of. 210
Gold, crystaloid solution of. 162
Gold figure. 80
Gold figure, determination of. 80
Gold ruby glass. 165
Graham's classification of colloids. 22
Graham's original nomenclature. 30
Graham's original paper on diffusion. 31
Graham's original paper on silicic acid. 47
Gum arabic, protective action of. 81, 87
Gum tragacanth, protective action of. 80, 81

Hæmoglobin. 206
Hardy's classification of colloids. 23
Heterogeneity of solutions. 3
Heterogeneity of crystalloid solutions, demonstration of. 6
Homogeneity of solutions. 3
Horse sera, examination of. 201
Hydrogel, definition of. 24
Hydrogels, formation of. 212
Hydrogels, remarks on. 227
Hydrogels, structure of. 116
Hydrosols, formation of. 212
Hydrosols, limits of size of particles in. 160
Hydrosols, nature of. 89
Hypomicrons, definition of. 110

Iodin suspension. 193
Irish moss, protective action of. 81
Irreversible hydrosols, definition of. 25
Irreversible colloids, definition of. 25
Irreversible hydrosols, effect of heat on the formation of. 223
Irreversible hydrosols, two classes of. 227
Isinglass, protective action of. 81, 87
Isoelectric state, Hardy's law of. 219

Jellies, formation of. 230

Maassen filter, experiments with. 153
Matter, colloidal condition of. 44
Mechanical subdivision, limitations of. 212
Metal fog. 70, 163
Metalumina, soluble. 40

PAGE
Micells, Nägeli's views on. 221
Microscopic resolvability. 101, 109
Microscopic visibility. 101
Milk, digestion of. 201
Molten salts, solubility of metals in. 1, 162
Mutual precipitation of colloids. 72

Optical constants, influence of cohesion on. 146
Osmotic method as applied to colloids. 90
Osmotic method, uncertainty of. 90

Pectization. 213
Peptization. 213
Peptones, action of, on colloidal gold. 82, 83, 85
Polarization of light by small particles. 115
Potassium subchlorid. 69
Precipitation of colloids by each other. 72
Protective action. 25, 148
Protective action of colloids:
    relative values of. 79
    variation of. 80
Protective action on suspensions. 86
Protective colloids. 77, 78, 79
Protective colloids, action of. 185
Pukall filters, experiments with. 153
Purple of Cassius. 65, 76

Red phosphorus, suspension of. 86
Reversible hydrosols, definition of. 25
Reversible colloids, definition of. 25
Reversible colloids, solution of. 213
Rice starch suspension. 195
Rubidium subchlorid. 69
Ruby glass. 165
Ruby glass, gold particles in. 165
Ruby glass, spontaneous crystallization in. 169
Ruby glass, technology of. 171

Selenium. 209
Sera, examination of. 201
Sera, gold figures of. 84
Silica, ultramicroscopic appearance of 231
Silicic acid, soluble. 35

PAGE
Silicic acid, Graham's research on..... 47
Silver chlorid suspension..... 194
Silver purple..... 70
Silver suboxid..... 74
Smoke, examination of..... 196
Sodium subchlorid..... 74
"Sol-formers"..... 126
Soluble starch, effect of heat on solutions of..... 224
Soluble starch, examination of..... 195
Soluble starch, size of molecule of..... 88
Solution, definition of.....8, 21
Solutions, heterogeneity of..... 3
Solutions, homogeneity of..... 3
Spontaneous crystallization..... 167
Stalagmometer, tests with.....83, 84
Stannic acid, pectization and peptization of..... 214
Stannic acids..... 71
Starch paste, ultramicroscopic examination of..... 196
Subdivision, definition of..... 9
Submicrons, definition of..... 110
Subchlorids..... 69
Sulphagels..... 51
Sulphur, separation of from thiosulphates..... 209
Supercooled solutions..... 167
Supersaturated solutions, starting crystallization in..... 222
Surface tension, effect of, on gel formation..... 232
Suspension, definition of.....9, 10, 22
Suspensions, contrasted with colloidal solution.....8–17
Suspensions and colloidal solutions, intermediate forms between.. 16
Suspensions, flocculation of.....13–15
Suspensions, ultramicroscopic examination of..... 193

Tetraiodofluorescein, examination of..... 197
Tin sesquioxid..... 71
Toxins and antitoxins, mutual actions of..... 73
Tragacanth, protective action of.....80, 81

Ultramarine suspension..... 58
Ultramarine, color of..... 146
Ultramicrons, color of..... 117
Ultramicrons, determination of size of..... 117
Ultramicrons, limit of visibility of..... 122
Ultramicrons, definition of..... 110

PAGE
Ultramicrons in gold hydrosols, relative size of. 157
Ultramicrons, motion of. 134
Ultramicroscope, description of. 103
Ultramicroscope, development of. 95
Ultramicroscope, manipulation of. 106, 111
Ultramicroscopic examination of fluids. 111
Ultramicroscopy, development of. 95
Ultramicroscopy, questions for. 92
Ultra-value, determination of. 202
Ultra-value of solutions. 199
Urine, ultramicroscopic examination of. 199, 200

Vapor pressure of metals. 163
Vegetable gum. 42

Water for ultramicroscopic uses. 208
Water, protective action of. 175
Water, purification of. 78
Weight, influence of, on suspended particles. 20
Wheys, electrolysis of. 202
Wheys, experiments with. 201

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